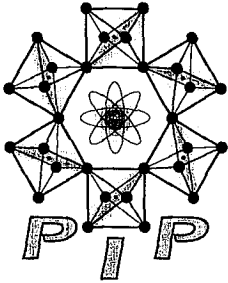**Fissile Materials Disposition Program**

Plutonium Immobilization Project
Baseline Formulation (U)

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1. Introduction and Summary

A key milestone for the Immobilization Project (AOP Milestone 3.2a) in Fiscal Year 1998 (FY98) is the definition of the baseline composition or formulation for the plutonium ceramic form. The baseline formulation for the plutonium ceramic product must be finalized before the repository- and plant-related process specifications can be determined. The baseline formulation that is currently specified is given in **Table 1.1**. In addition to the baseline formulation specification, this report provides specifications for two alternative formulations, related compositional specifications (e.g., precursor compositions and mixing recipes), and other preliminary form and process specifications that are linked to the baseline formulation. The preliminary specifications, when finalized, are not expected to vary tremendously from the preliminary values given herein.

Table 1.1 The Baseline Formulation.

Oxide	Baseline (wt%)
CaO	9.952
HfO_2	10.653
UO_2	23.690
PuO_2	11.892
Gd_2O_3	7.951
TiO_2	35.862
Pu	10.488

Because of the cooperation and team work of the participating sites involved in this work—Lawrence Livermore National Laboratory (LLNL), Savannah River Site (SRS), Australian Nuclear Science Technology Organization (ANSTO), Argonne National Laboratory (ANL), and Pacific Northwest National Laboratory (PNNL)—a large number of samples have been generated and analyzed, thus making it possible to finalize the baseline formulation at this time with good confidence. The baseline formulation has been shown to be:

- Very resistant to chemical dissolution in repository-like environments

- Safe with respect to short- and long-term nuclear criticality in preliminary repository degradation analyses

- Able to accommodate PuO_2 feed impurities in the ranges expected

- Amenable to fabrication processes similar to those found in the mixed oxide (MOX) nuclear fuel industry.

2. Form Development Strategy

2.1 Plutonium Feed Assumptions

The Department of Energy Materials Disposition Program (DOE-MD) within the Office of Fissile Materials Disposition will be receiving fissile materials packaged by facilities operated for the Offices of Defense Programs (DOE-DP), Environmental Management (DOE-EM), and Nuclear Energy (DOE-NE). These materials are to be dispositioned in a manner that meets the "spent fuel standard" (i.e., one that "make[s] the weapons-usable plutonium roughly as unattractive and as inaccessible for retrieval and weapons reuse as the residual and growing stockpile of plutonium in spent fuel from commercial reactors"). At the present time, approximately 18 metric tonnes of relatively impure plutonium are targeted for disposition by immobilization and approximately 32 metric tonnes of relatively pure plutonium from decommissioned nuclear weapons are targeted for disposition as MOX fuel in existing light water reactors. If political or economic factors for the MOX approach cannot be satisfied, the option exists to disposition the entire 50 metric tonnes of plutonium by immobilization.

2.1.1 Feed Materials

The compositions, forms, and storage packages of surplus-plutonium-bearing materials throughout the complex are not well defined. The majority of the separated plutonium that is not in nuclear weapons components is housed in the production plants—Rocky Flats, Hanford, and Savannah River—in conditions that are not acceptable for long-term storage. These materials will require repackaging; some will require stabilization or minimal processing to allow safe storage until disposition is complete. Until 1994, complex-wide directives that applied to plutonium storage, including safety and safeguards orders, were general in nature. Therefore, current plutonium storage practices vary among sites. These directives do not provide much detail on how plutonium should be prepared for storage, in what sort of containers it should be placed, and how the containers should be monitored.

Chemical data for the plutonium feedstock targeted for disposition vary in completeness but approximate groupings are as follows:

- *Group I*—Materials with purity far exceeding what is required for immobilization: approximately 45 tonnes for the 50-tonne case, or approximately 12 tonnes for the 18-tonne case.

- *Group IIa*—Materials with relatively low impurity levels that can be used directly or may be easily blended into acceptable feed stocks for immobilization: approximately 3 tonnes.

- *Group IIb*—Materials with higher levels of specific impurities that require some treatment before blending to remove or deplete the impurities of concern. These materials, approximately 1 tonne, will be handled in the Immobilization Conversion Facility. (These include the "chloride oxides" at Rocky Flats and Hanford.)

- Group IIIa—Materials previously identified by internal DOE studies as requiring processing in the SRS canyon (aqueous dissolution and reprecipitation): approximately 1 tonne. These materials include fluoride materials and scrub alloy at Rocky Flats as well as sand, slag, and crucible materials at both Rocky Flats and Hanford. (After processing at Savannah River, these Group IIIa materials will move into Group I.)

- Group IIIb—Salt residues from molten salt processing: approximately 1 tonne. These have been previously identified as needing removal of the chloride salts for stabilization purposes. (After removal of about 75% of the 16 tonnes of spent chloride salts, this material would meet the description of Group IIa.)

- Group IIIc—A group of materials with plutonium contents as low as 5 wt%. These materials may be dispositioned in some other manner, but could ultimately end up as a feed stream at the Plutonium Immobilization Plant (PIP).

2.1.2 Impurities and Isotopics

The isotopic composition of the 50 tonnes of excess plutonium feed stock vary from 3% ^{240}Pu to approximately 40% ^{240}Pu. The plutonium assay in the candidate materials varies from under 10 wt% to over 99 wt%. The last date of purification of these materials varies from the early 1960s to the late 1990s. Therefore, the ^{241}Am content varies from as little as 200 ppm for the recently purified materials to as much as 20 wt% for some of the older reactor grade or americium-enriched materials. The uranium content varies from trace depleted uranium in the plutonium to trace plutonium in fully enriched (93% ^{235}U) uranium. A summary of the average and extreme impurity amounts in the PuO_2 feed is given in Table 2.1. An average impurity concentration is also given in the table for the impure oxides. In general, the impurities in the existing feed stock contain the following elements: aluminum, carbon, calcium, chlorine, iron, fluorine, gallium, potassium, magnesium, molybdenum, sodium, silicon, tantalum, uranium, and tungsten. Note that for the maximums given in **Table 2.1**, the total exceeds 100% because the maximum for each element generally occurs in different feed streams.

With the possible exceptions of carbon and the halides (chlorine and fluorine), fairly high levels of all the impurities listed in Table 2.1 are tolerated by the immobilization form. Feed blending is required for the more extreme cases to create impurity concentrations closer to the average. Before the feeds are blended and then immobilized, high carbon contents need to be removed or depleted and high halide contents should also be removed or depleted.

2.2 Repository Requirements

The immobilization form must provide adequate performance in a geologic repository and be capable of qualification for acceptance by a repository. This implies that the form must:

- Incorporate sufficient insoluble neutron absorber(s) to assure long-term criticality safety

Table 2.1 Average and Extreme Impurity Contents in the PuO$_2$ Feed.

Impurity	Average Feed (wt%)	Average Impure Oxide (wt%)	Max. All Feeds (wt%)	Impurity	Average Feed (wt%)	Average Impure Oxide	Max. All Feeds (wt%)
Al	1.58	5.29	7.94	Mo	0.50	0.54	2.39
Am	1.74	0.00	4.00	Na	0.71	1.18	2.36
B	0.13	0.22	0.77	Ni	0.28	0.94	2.67
Ba	0.53	0.45	4.48	Nd	1.03	0.00	12.57
Be	0.00	0.00	0.00	Np	0.41	0.00	3.20
C	1.99	4.50	40.68	P	0.01	0.00	0.69
Ca	2.14	8.80	48.34	Pb	1.98	0.00	10.65
Cd	0.00	0.00	0.00	Si	1.70	4.10	26.38
Ce	0.62	0.48	2.16	Sn	0.02	0.00	0.23
Cl	1.76	2.92	12.37	Ta	0.27	0.75	6.07
Cr	0.14	0.42	1.37	Th	0.00	0.00	0.01
Cu	0.43	0.00	2.67	Ti	0.07	0.00	2.07
F	2.06	1.46	29.94	U	20.92	0.00	68.39
Fe	0.60	1.64	5.66	V	0.00	0.00	0.00
Ga	1.19	0.00	9.55	W	0.06	0.00	2.16
Gd	0.11	0.00	0.59	Zn	0.20	0.00	2.25
Hf	0.83	0.00	0.63	Zr	0.00	0.00	0.02
Hg	0.00	0.00	0.00				
K	0.77	3.28	7.95	Pu	38.67	38.96	88.20
La	0.06	0.09	1.71	O	15.41	21.55	101.92
Mg	1.08	2.42	22.49				
Mn	0.00	0.00	0.07	Total	100.00	100.00	535.60

- Be sufficiently durable, with respect to aqueous corrosion, under repository disposal conditions

- Not have a deleterious effect on the repository performance of the surrounding vitrified high level waste (HLW) (assuming the can-in-canister disposition alternative)

- Withstand the thermal cycle associated with the HLW canister cool-down with no adverse effects on performance or the capability to qualify the waste

- Meet the other applicable requirements for a waste form in a geologic repository as specified by regulations and repository acceptance documents.

2.2.1 Criticality Safety and Durability

If arranged in a suitable configuration, the quantity of plutonium in an HLW canister of the current can-in-canister design is more than sufficient for nuclear criticality to occur. It is therefore necessary to prevent this by the addition of suitable neutron absorbers. Ideally, one would choose a neutron absorber that has chemical characteristics identical to plutonium so that ceramic degradation and transport processes will not separate the plutonium and absorber from one another. Unfortunately, such a material does not exist. One can, however, choose

to incorporate neutron absorbers that are known to be relatively insoluble in groundwater and will therefore remain in the waste package should the ceramic eventually degrade.

In the long term, of course, the plutonium will decay, primarily to the fissile nuclide ^{235}U. In the case of uranium, it is possible to add the non-fissile ^{238}U to isotopically "dilute" the ^{235}U. The current ceramic formulation does involve addition of depleted or natural uranium. Although it is not economically feasible to add sufficient ^{238}U to preclude criticality, the added uranium does assist in making far-field criticality even less likely by increasing the quantity of uranium that must be transported and then reprecipitated in a configuration free from any of the added neutron absorbers.

As fabricated, the proposed ceramic formulation is criticality-safe in any config-uration, even when optimally moderated. As long as the form stays reasonably intact, then, criticality safety is assured. It is only when the form begins to degrade by contact with groundwater in a repository that there can be a ques-tion of criticality safety. The rate and mechanism by which the ceramic degrades are thus intimately related to the question of long-term criticality safety. Obviously, the more durable the material, the longer one can be assured of criti-cality safety; however, there are no simple measures of "sufficiency" for either neutron absorber content or ceramic degradation rate. The envelope of accept-able composition and performance can only be determined by analysis. The Department of Energy Office of Civilian Radioactive Waste Management (OCRWM) and its contractors are performing such analyses. Their latest series of criticality analyses were conducted using a ceramic composition and plutonium loading consistent with those given in this report. The relative degradation rates of the ceramic, HLW glass, and container were varied independently, within realistic limits based on existing data. These analyses showed no physically real-izable scenarios in which a nuclear criticality was possible.

2.2.2 Compatibility with High-Level Waste (HLW) and the Can-in-Canister Configuration

Both the ceramic form and the associated hardware used to contain it in the can-in-canister configuration must be compatible with the vitrified HLW and its can-ister. Here, compatibility is taken to mean that the can-in-canister materials do not impede the pour of the HLW glass melt into the canister, that they do not react with the melt or glass, and that they do not have a deleterious effect on the performance of the HLW glass under repository conditions. Conversely, the ceramic must be chosen such that the glass does not have a deleterious effect on the performance of the ceramic.

Tests are being conducted as part of the performance testing effort of the research, development, and testing (RD&T) program to demonstrate that such undesirable interactions do not occur. Testing to date indicates that the ceramic degrades at a rate so much slower than the glass that it can be considered inert from the standpoint of the glass. Similarly, it is not expected that the degradation of the glass will affect the degradation rate of the ceramic. It is possible, however, that colloidal material produced by the alteration of the HLW glass could pro-vide a transport mechanism within the repository for surface-active species such as plutonium. Such an interaction, however, would exist for any waste form chosen for plutonium disposition in the can-in-canister configuration.

In addition to chemical considerations, the ceramic form must be capable of withstanding the thermal cycle associated with the HLW canister cool-down with no adverse effects on performance or on the capability to qualify the waste. Thermal cycling tests conducted with early versions of the current ceramic formulation indicate that no detectable changes occur in mineralogy, chemistry, or grain size of ceramics subjected to simulated cooling histories. Some cracking of the pellets due to thermal shock may occur. The extent to which this occurs will need to be quantified and reported to the repository, as fracturing will change the exposed surface area of the ceramic.

2.2.3 Other Repository Requirements

The current Nuclear Regulatory Commission (NRC) regulation governing the licensing of a high-level nuclear waste repository is 10 CFR 60.* This code specifies certain requirements on repository subsystems, including several design requirements that pertain specifically to the contents of the waste packages (including the waste forms). These requirements are that to the extent that organic materials, free liquids, or explosive, pyrophoric or combustible materials might compromise the ability of the disposal system to isolate waste, the waste package cannot contain them. The ceramic proposed for plutonium disposition will easily meet these requirements.

In addition to the regulatory requirements of Part 60, the repository program also requires that any waste form be free of hazardous materials. Specifically, the producer must determine and report to DOE-EM and OCRWM the presence or absence of any hazardous waste (listed in 40 CFR 261.31 through 40 CFR 261.33) in the waste. Any Resource Conservation and Recovery Act listed (RCRA-listed) component in the waste requires the producer to petition the Environmental Protection Act (EPA) and receive exemption to delist the waste.

The producer must also perform appropriate tests and procedures (as described in 40 CFR 261.20 through 40 CFR 261.24) using samples from production runs or prototypical specimens to determine if the immobilized form that will be received by the repository has hazardous characteristics. Any waste that is shown to have hazardous characteristics must be treated to remove such characteristics.

2.3. Evolution of the Immobilization Form and Process

The ceramic form and process for immobilization of excess plutonium has evolved considerably since the summer of 1995 when they were first conceived. The initial ceramic form considered was synthetic rock (SYNROC), specifically, SYNROC-C.2 This is composed of roughly equal amounts of zirconolite, perovskite, and hollandite with lesser amounts of rutile and noble

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* The NRC is currently in the process of revising Part 60, and is expected to promulgate new regulations (10 CFR 63) that will supersede Part 60 for the case of licensing a repository at Yucca Mountain. The draft of Part 63, which is currently under review, does not include the subsystem specifications and requirements present in Part 60. Requirements are only placed on the system as a whole. Although the regulatory basis for the waste package design requirements may disappear, the requirements are reasonable and will probably be maintained as requirements imposed by the repository program itself.

metal alloys. SYNROC (which is short for SYNthetic ROCk) was initially designed for the immobilization of HLW.3 A variety of SYNROC variants have been proposed.3-10 **Table 2.2** summarizes all of the SYNROC forms that have been studied to date. The SYNROC methodology has also been used to develop a form to immobilize mixed wastes and, in this program, a form to immobilize actinide-rich wastes. The mixed-waste ceramic and the plutonium ceramic variants are also shown in Table 2.2 for comparison.

Table 2.2 Summary of SYNROC and Related Variants.

Form Name	Mineralogy (wt%)	"Waste" Loading	Fabrication Process
SYNROC-A	40% Ba-feldspar, 30% hollandite, 20% perovskite, 10% zirconoia, kalsilite, and/or leucite	10% HLW	Melting and crystalizing 1330°C
SYNROC-B	40% hollandite, 35% zirconolite, 25% perovskite,	None	Hot pressing 1200-1400°C
SYNROC-C	33% hollandite, 28% zirconolite, 19% perovskite, 15% rutile, 5% noble metal alloy	20% HLW	Hot pressing 1150°C
SYNROC-D	46% spinel solid solution, 19% zirconolite, 17% nepheline, 15% perovskite, 3% hollandite	63% HLW sludge	Hot pressing 1050-1100°C
SYNROC-E	79% rutile, 7% zirconolite, 7% perovskite, 5% hollandite, 2% pyrochlore	7% HLW	Hot pressing 1300°C
SYNROC-F	90% pyrochlore, 5% hollandite, 5% rutile	50% U-rich HLW	Hot pressing 1250°C
SYNROC-FA	89% pyrochlore, 8% perovskite, 3% uraninite	50% U-rich HLW	Cold pressing and sintering 1250-1400°C
Mixed Waste Ceramic	36% nepheline, 31% spinel solid solution, 12% zirconolite, 12% perovskite, 5% rutile, 4% calcium phosphate	40% residue	Cold pressing and sintering 1150-1200°C
Pu Ceramic Zirconolite-rich	80% zirconolite (with some pyrochlore) 10% hollandite, 10% rutile,<1% PuO_2	12% Pu	Cold pressing and sintering 1325-1400°C
Pu Ceramic Pyrochlore-rich	85% pyrochlore, 10% brannerite, 5% rutile, <1% uraninite solid solution	10.5% Pu and21% U	Cold pressing and sintering 1275-1400°C

Of all the SYNROC formulations, SYNROC-C is by far the most studied and probably the most developed. The strategy underlying SYNROC is to immobilize the radioactive isotopes of HLW in a mixture of minerals that all have natural analogs that:

- Have survived for periods exceeding 20 million years in a wide variety of geochemical environments

- Have crystal chemical properties that allow them to accept a wide range of elements into their crystalline matrix

- Are thermodynamically stable together.

A wide range of minerals meet these three criteria. Titanate-rich minerals were selected because they not only meet the above criteria, but they are composed of one of the most insoluble oxides known, namely TiO_2.

Actinides are components of HLW that are easily accommodated into SYNROC. Consequently, SYNROC was also an attractive candidate for the narrower problem of immobilizing excess plutonium. For the HLW application, the SYNROC product was to be prepared by using alkoxide and nitrate precursors and fabricated by hot uniaxial pressing (HUP) in stainless steel bellows. The bellows are necessary to prevent the volatilization of some HLW species such as ^{137}Cs during processing. Because it had already received a considerable amount of development and testing, the same process was initially selected for the plutonium immobilization application. Each ceramic disk produced would have weighed roughly 30 kg. This was about the largest size demonstrated in the late 1980s at the ANSTO SYNROC Demonstration Plant in Lucas Heights, Australia.[11]

Two ceramic options were initially considered for disposition of excess plutonium. The first was a homogenous form in which both plutonium and radioactive cesium were contained in the ceramic matrix. The second was a heterogeneous form in which a plutonium-loaded ceramic interior form was embedded in HLW glass containing radioactive cesium (i.e., the "can-in-canister" option). Due largely to technical risk, cost, and schedule considerations, the heterogeneous can-in-canister option was selected for implementation[x]. The ceramic form was subsequently chosen over LABs glass as the immobilization matrix[y].

Over the past three years, the formulation has evolved from SYNROC-C to a pyrochlore-rich form that contains some brannerite, zirconolite, and rutile. During the same time, the hot pressing in bellows operation has been replaced by a simpler cold pressing and sintering operation similar to that used in the MOX industry.

2.3.1 Mineralogical Selection

The SYNROC-C formulation would probably have been adequate for the plutonium disposition mission. However, it was originally designed and optimized for immobilization of HLW, not for the immobilization of plutonium-rich wastes. When the constituents of concern are mainly actinides (namely plutonium), the form is easily tailored to better meet the assumptions and goals of the plutonium disposition mission. As assumptions and goals have evolved since the program's inception, so has the formulation evolved.

In SYNROC-C, both zirconolite and perovskite are the host phases for the actinides. Because perovskite is known to be considerably less durable than zirconolite,[12] perovskite was eliminated from the baseline plutonium ceramic and zirconolite was maximized to about 80 wt%. Because the plutonium feed stream does not contain any noble metal fission products, the noble metal alloys were also eliminated from the plutonium ceramic. Hollandite is a host for cesium and barium. Radioactive cesium was the gamma radiation source for homogenous form. Except for the small radioactive cesium in the form of Cs_2O, the same formulation was initially proposed for both the homogenous ceramic and the inner form in the heterogeneous (can-in-canister) form. Barium in the form of BaO was needed to stabilize the hollandite phase and was also needed as a sintering aid in this formulation when the fabrication route was cold pressing and sintering. The initial product was thus designed to contain about 15 wt% hollandite. Rutile provides a compositional buffer that can react with and immobilize unanticipated impurities in the feed. The product was thus designed to contain about 5 wt% rutile.

The as-fabricated product had to be criticality safe in any configuration that might be used to load the HLW canister. As a result, neutron absorbers had to be included in the form. The rare earths (samarium, gadolinium, and europium) were selected as the preferred neutron absorbers because they were easily accommodated in large amounts into the plutonium ceramic form, and because they are considerably less soluble in groundwater environments than other commonly used neutron absorbers such as lithium, boron, and cadmium. Of the three rare earth elements (REEs) considered, gadolinium was selected as the preferred neutron absorber. Europium is much more expensive than samarium or gadolinium, and gadolinium is recognized to be the most effective absorber of thermal neutrons, which is important for preventing criticality events in heavily moderated environments. At the time, it was not known how much neutron absorber would be required for criticality control. A one-to-one atomic ratio of gadolinium-to-plutonium was rather arbitrarily selected and later confirmed to be more than adequate in the as-fabricated form.

The plutonium loading was also selected rather arbitrarily. The loading level selected dates back to the original conception of the form and process for the plutonium disposition application in the summer of 1995. It was known from previous work at ANSTO that the form could easily accommodate more than 10 wt% plutonium. The maximum size of the hot-pressed product demonstrated at ANSTO was around 33 kg and typical glovebox limits for plutonium processing would likely be around 4 kg. The form was thus selected to contain 12 wt% plutonium, a number arrived at by dividing 4 kg plutonium by 33 kg of ceramic. Given all of the above considerations, the overall formulation was designed as follows:

80 wt% zirconolite ($Ca_{0.75}Gd_{0.25}Zr_{0.75}Pu_{0.25}Ti_2O_7$)

15 wt% hollandite ($Ba_{1.14}Al_{2.29}Ti_{5.71}O_{16}$)

5 wt% rutile (TiO_2).

The above formulation was then used to calculate the amounts of the precursor components to be mixed together and processed. The fabricated product matched the design mineralogy reasonably well, although traces of pyrochlore were also

present. The rutile content appeared to be slightly greater than 5 wt% and the hollandite content appeared to be slightly less than 15 wt%. The theoretical density was calculated to be 4.92 g/cm^3. The actual geometric density observed was about 4.5 g/cm^3. This initial formulation is now referred to as the zirconolite-based form. A secondary electron image (SEI) of the zirconolite-rich plutonium ceramic form is shown in **Figure 2.1**.

The initial formulation assumed relatively pure PuO_2 as the feed stream. After this initial idealistic assumption was corrected and the preliminary compositions of the actual feed streams became available, it was apparent that the feed streams targeted for immobilization had on average about equal amounts of uranium (primarily natural and depleted uranium) and plutonium. If the plutonium-loading in the form were to remain at about 12 wt%, the excess uranium would stabilize considerable amounts of pyrochlore in the product. The potential for uranium-rich HLW had already lead to the development of pyrochlore-rich SYNROCs called SYNROC-F[8] and SYNROC-FA[9] (see Table 2.2).

At about the same time as the more realistic feed compositions were being assembled, questions about the radiation damage effects in the ceramic form were raised. An initial conservative long-term degradation analysis performed by OCRWM assumed that after a few thousand years, swelling caused by alpha decay of the plutonium in the ceramic would make the zirconolite-rich ceramic fracture into a powder at the gain boundaries.[13] The same analysis by OCRWM[13] indicated that under worst case assumptions the gadolinium could become soluble, and that a small concentration of the insoluble neutron absorber

Pyrochlore

Zirconolite

Hollandite

Actinide Oxide

Rutile

20 μm
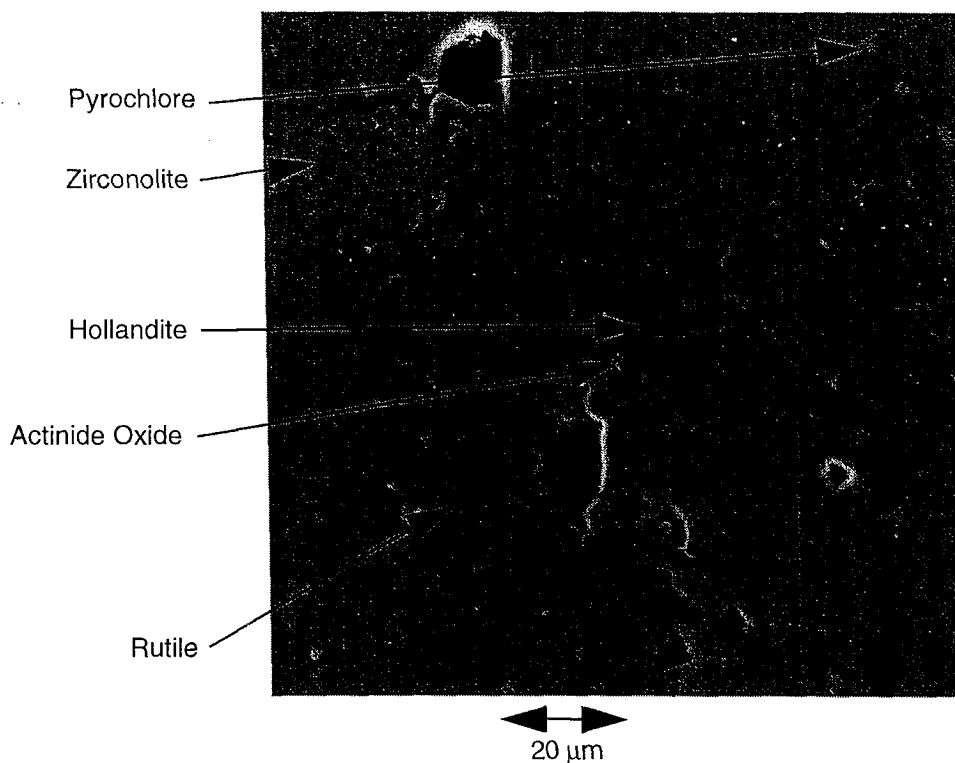
Figure 2.1 Secondary electron image of zirconolite-rich form loaded with 12 wt% plutonium.

hafnium could prevent criticality. In particular, the small amount of hafnium present as a contaminant in zirconolite (2 to 5% of total zirconium) was found to increase, by 50%, the amount of ^{239}Pu that could be carried in a waste package without permitting criticality. It was clear that the ceramic form would benefit by redesigning the formulation.

On April 8, 1997, a videoconference among LLNL, SRS, and ANSTO was held to discuss the redesign of the ceramic formulation and generation of an initial impurity test matrix (later called the Series A matrix[14]). The following criteria were agreed upon:

- Uranium-to-plutonium ratio of 2-to-1 (exceeds uranium content in most feed streams)

- Gadolinium-to-plutonium ratio of 1-to-1 (same as in zirconolite-rich formulation)

- Hafnium-to-plutonium ratio of 1-to-1 (replace zirconium with hafnium and select 1-to-1 ratio as was done with gadolinium to provide additional criticality control)

- Eliminate BaO and hollandite from the form (no RCRA material)

- For purposes of calculating the feed composition, assume a pyrochlore form with a small amount of hafnium-rutile (95 wt% pyrochlore, 5 wt% hafnium-rutile)

- Plutonium concentration about the same as in the zirconolite-rich form (reduced to about 10 wt% due to higher density of pyrochlore).

Given the above criteria, the form was designed as follows:

95 wt% pyrochlore ($Ca_{0.89}Gd_{0.22}Hf_{0.23}U_{0.44}Pu_{0.22}Ti_2O_7$)

4 wt% rutile (TiO_2)

1 wt% hafnia (HfO_2).

Note that extra hafnia was added because the rutile in the zirconolite-rich formulation was known to contain about 6 mol% zirconia. In the absence of experimental data, hafnia was expected to behave similarly and substitute into the rutile. Given the differing molecular weight of hafnium versus zirconium, the HfO_2 to TiO_2 weight ratio in the hafnium-substituted rutile was expected to be about 1-to-4. The theoretical density was calculated to be 5.98 g/cm^3. The actual geometric density observed was about 5.5 g/cm^3.

As planned, pyrochlore was the primary phase and rutile was present in small amounts. However, the actual form produced varied slightly from the designed mineralogy in the respect that brannerite was also formed. If impurities were present, zirconolite also formed. Although this result was slightly different than expected, zirconolite and brannerite were known or expected to be durable phases and both had natural mineral analogs that have survived over geologic time periods. Therefore, it was decided to leave the formulation as it was and, if

needed, redesign it slightly at a later time. By allowing a relatively wide range of pyrochlore, zirconolite, and brannerite mineral abundances in the product, the form was much more tolerant to impurities in the PuO_2 feed than a form targeting a nominally single-phase product.

The baseline product produced from this formulation is shown in **Figure 2.2**. The actual product formed was composed of about 80 wt% pyrochlore with the balance being roughly equal amounts of brannerite and rutile. Since the April 1997 videoconference, the composition of the baseline form has remained essentially unchanged. At a form development meeting at LLNL on June 9 and 10, 1998, the baseline formulation was reviewed. It was noted that the form could be made more tolerant to impurities by increasing the hafnium-rutile content in the form, but for the current plutonium disposition mission the formulation did not need to be redesigned.

2.3.2 Processing Considerations

As mentioned earlier, the ceramic product was originally conceived to be fabricated as hot-pressed disks weighing about 30 kg each. These disks were planned to be about 1 foot in diameter by about 3.5 inches high. Due largely to their size and shape, these disks presented some engineering problems for the preferred can-in-canister immobilization option. The main problem was that the cross-sectional area of the disks was too large to allow unobstructed flow of the HLW glass into the canister. The initial solution was to scale down the size of the hot-pressed disks, but this was expected to significantly reduce the cost effectiveness of the proposed process. There were two alternatives. One alternative was to use hot isostatic pressing (HIP) rather than HUP. The HIP product could be made in
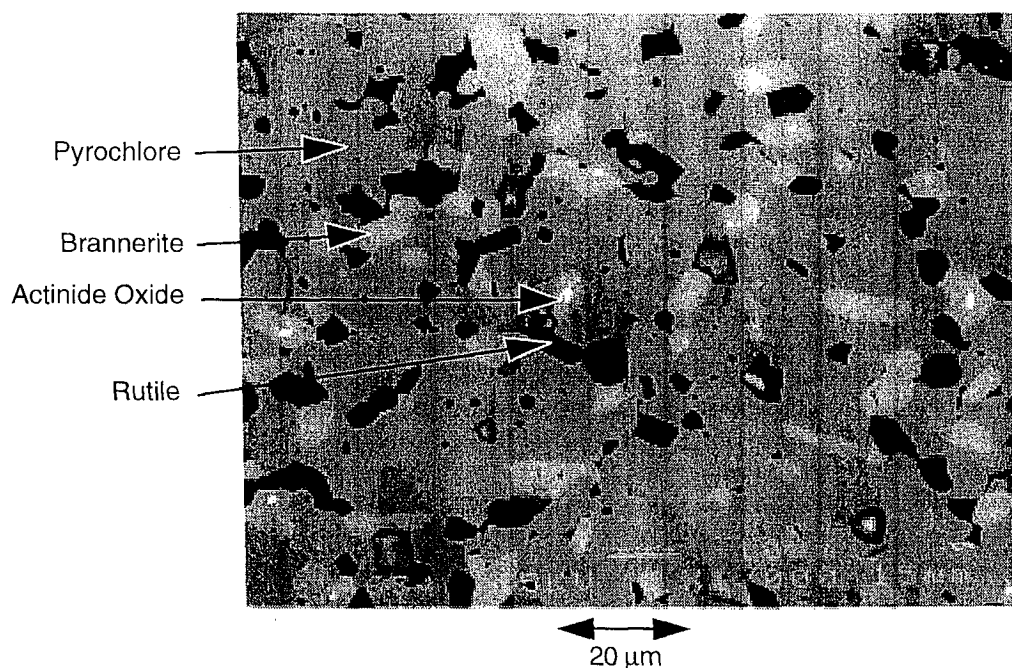
Figure 2.2 Baseline electron image of pyrochlore-rich form loaded with 10.5 wt% plutonium.

a can shape (long and slender rather than thin and wide), eliminating the obstruction of the molten HLW glass during the HLW glass-filling operation. The other alternative was to go to a cold pressing and sintering approach that was based primarily on the MOX industry. Data were already available showing that cold pressing and sintering could be used to fabricate SYNROC-FA, which is similar in composition to the pyrochlore-rich plutonium ceramic form. Based on favorable tests performed in the early years of the program, the cold pressing and sintering option was quickly selected as the preferred option. The HIP option, which was maintained as a backup for a short period of time, is no longer being considered.

Although there are several well-developed processes for fabricating MOX pellets, the specific processes used for the ceramic form differ somewhat and require development and testing to prove that the processes will be suitable for the proposed Plutonium Immobilization Plant.

There are substantial differences between the ceramic immobilization product and the MOX product in terms of size and composition of the product form. The nominal size of the ceramic product was selected to be approximately 2.5 inches in diameter by approximately 1 inch high. Based on discussions with several ceramic engineers and suppliers of automated presses, this was believed to be a reasonable upper bound in size that could be fabricated reliably by an automated process using cold pressing and sintering.

The most important steps in the fabrication process, in terms of impact on the final form, are the milling step, the blending/mixing step, the pressing step, and the burnout and sintering step. Considering the processes developed and used for the MOX industry, there are two preferred options for the milling and blending/mixing steps. One method involves the use of sequential attritor mills and the other involves the use of ball mills. The processing route using sequential attritors was developed by British Nuclear Fuels Limited (BNFL) and is commonly referred to as the "Short Binderless Route."[15, 16] The process using ball mills was developed at Belgonucleaire and Cogema and is commonly referred to as the "Mimas" process.[17] The sequential milling and blending/mixing process with attritor mills is the baseline process for the plant. Dry ball-milling or dry ball-blending/mixing was not selected since such milling has already been demonstrated to be relatively ineffective for milling or blending/mixing either the actinides or the precursors. Wet ball-milling and blending is an effective process, but would require additional water removal operations.

Pressing is performed at very low pressures compared to those used in the MOX industry and many other ceramic fabrication processes. Using ungranulated precursor material, pressures as low as 1000 psi have been demonstrated to be adequate for this form and process. Granulated material generally requires higher pressing pressures to obtain high pellet densities and good pellet integrity. The pellet press will be specifically designed for this process, but will probably be very similar to those used in the MOX industry.

For the binder burnout and sintering step, two types of furnaces were considered: a bottom-loading furnace and a conveyer-type furnace. The conveyer furnace is often preferred for the MOX industry. However, the larger immobilization ceramic

"pucks" required a slower heating and cooling rate to avoid fracture. As a result, a high-temperature bottom-loading furnace is currently believed to be more suitable for the ceramic immobilization plant.

The sintering temperature initially selected was 1325°C for 1 hour. For earlier zirconolite-based formulations, good densities at lower temperatures and shorter times could not be achieved. Experiments on actinide oxide reaction kinetics on the zirconolite-based formulation indicated that a firing temperature of 1350°C for 4 hours was required to get good reaction of PuO_2 particles that are initially less than 20 microns with the ceramic matrix. Later experiments on the pyrochlore-based form indicated that lower temperatures could probably be used, but 1350°C for 4 hours has been retained as the baseline.

The sintering atmosphere was initially selected to be argon gas. Recent experiments on the pyrochlore-based form indicate that air is a suitable sintering atmosphere. Since air is cheaper and easier to use than argon, the preferred sintering atmosphere is now air.

3.   Sample Test Plan

3.1 Program Overview

Development of the baseline formulation and baseline process operations are coupled; one cannot be complete without the other. More specifically, the baseline formulation has been designed so that the desired product mineralogy is obtained, but the fabrication process (still under development) can also affect product mineralogy.

The form development sample test plan was designed to understand how the baseline formulation selected on the April 9 video conference[13] was affected by various compositional and processing parameters. As a result of the tests conducted so far, the formulation has been verified to be suitable for the types of compositional and process variations that would be expected in the Plutonium Immobilization Plant. If the baseline formulation had been determined to be lacking in a needed or desirable attribute, it would have been redesigned. At this point, however, sufficient testing has been completed to allow the baseline formulation to be finalized.

3.1.1 Form Development Tasks

Form Development is divided in four primary task areas. The main objectives according to each task are shown below in bulletized form.

Task 1. Planning and Facilities

- Establish capabilities for small-scale sample fabrications.

- Define the sample test matrix.

Task 2. Process Data

- Define the baseline formulation.

- Provide feed specifications for the PuO_2 feed.

- Provide process data that supports scale up testing and design.

Task 3. Form Qualification Samples

- Provide samples for durability testing.

- Provide samples for thermodynamic data measurements.

- Provide range and composition of minerals in the ceramic form.

Task 4. Product Control Model Development

- Develop a product control model to qualify the fabrication process.

3.1.2 Participants and Capabilities

The Form Development participants are LLNL, ANSTO, SRS, and ANL. Pacific Northwest National Laboratory is involved peripherally due to their efforts in fabricating the radiation damage test samples. All of the sites mentioned above have capabilities to make small-scale plutonium-loaded samples. The types of samples being prepared at each site are dependent largely upon the characterization equipment available at the site and whether or not any subsequent tests (e.g. durability, thermochemical, and nondestructive evaluation [NDE] tests) will be performed at the site. Note that some redundancy is built into the plan, particularly for high priority samples needed for durability testing. For the most part, analytical capabilities are equivalent at all of the sites for the non-plutonium work.

As shown in **Table 3.1**, there are significant differences, however, in readily available analytical equipment to perform analyses on plutonium-loaded samples. For example, ANSTO and SRS are best set up to perform x-ray diffraction work. Lawrence Livermore National Laboratory has the only capability for compositional analysis using an electron microprobe. All the sites have scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) capability, but ANSTO has the most complete selection of standards suitable for quantitative SEM/EDS work on the plutonium-loaded ceramics. Argonne National Laboratory and ANSTO are best set up to perform transmission electron microscopy (TEM) work. Argonne National Laboratory is performing a large fraction of the durability tests. Consequently, many of the samples needed for durability testing are being fabricated at ANL. Savannah River Site and ANSTO are currently best set up for getting immersion densities. However, this capability is relatively easy to install. Lawrence Livermore National Laboratory currently has the only capability to perform particle size analysis on plutonium-containing materials. With some effort, plutonium-samples can be shipped between all of the DOE sites. However, shipment of plutonium samples from ANSTO to any of the DOE sites or from any of the DOE sites to ANSTO is extremely difficult except in trace quantities.

Table 3.1 Readily Available Analytical Capabilities for Plutonium-Loaded Samples.

Analytical Capability	Sites with Readily Available Capabilities for working with Pu-loaded Materials[a]
X-ray Diffraction Analysis	ANSTO, PNNL, and SRS[b]
Quantitative Microprobe Analysis	LLNL
Quantitative EDS Analysis	ANSTO[c]
TEM Analysis	ANL and ANSTO
Immersion Density	ANSTO, PNNL, and SRS
Durability Testing Analyses	ANL[d]
Particle Size Analysis	LLNL

[a]Note that all sites have additional plutonium capabilities that may be of interest (not listed).

[b]ANL and LLNL also have plutonium/x-ray diffraction capabilities. The LLNL equipment needs to be serviced to perform better. The ANL equipment is outside of the normal plutonium processing area.

[c]ANL, LLNL, PNNL, and SRS all have EDS capabilities that could be made quantitative with a better selection of standards that closely match the compositions of the minerals in the ceramic product.

[d]LLNL, PNNL, and SRS are also involved in a smaller suite of durability tests.

3.2 Sample Test Matrices

The sample test matrices were first developed in late December 1997 at a review meeting at SRS. The sample test matrices were reviewed again and updated at a program-wide form development planning and review meeting at LLNL in early June of 1998. The detailed test matrices as they currently stand are given in Appendix A. The A series originated in FY97 and the B series originated in FY98. The C series is planned to begin early in FY00. The series A samples are for the most part complete. The B series samples are in progress, and are nominally about half-complete. Note that each sample series usually corresponds to a single composition, but in some cases it corresponds to a range of compositions or impurity loading levels. For each composition identified, several to approximately a dozen samples are prepared. Some are sintered at different temperatures or under different atmospheres. Some are fabricated by different processes, and so on.

Note that the sample series support multiple tasks. The linkages between the sample test matrices and the tasks are shown in **Figure 3.1**. In general, each series supports primarily one task (the solid lines) and peripherally at least one of the other tasks (dashed lines).

The development, testing, and finalization of the baseline formulation is dependent at least to some extent upon all of the sample series. However, the main sample series that support the finalization of the baseline formulation are the A series, B1 series, B4 series, and B5 series. Although the B series are not complete, sufficient data have been generated to initially validate the current baseline formulation selection.
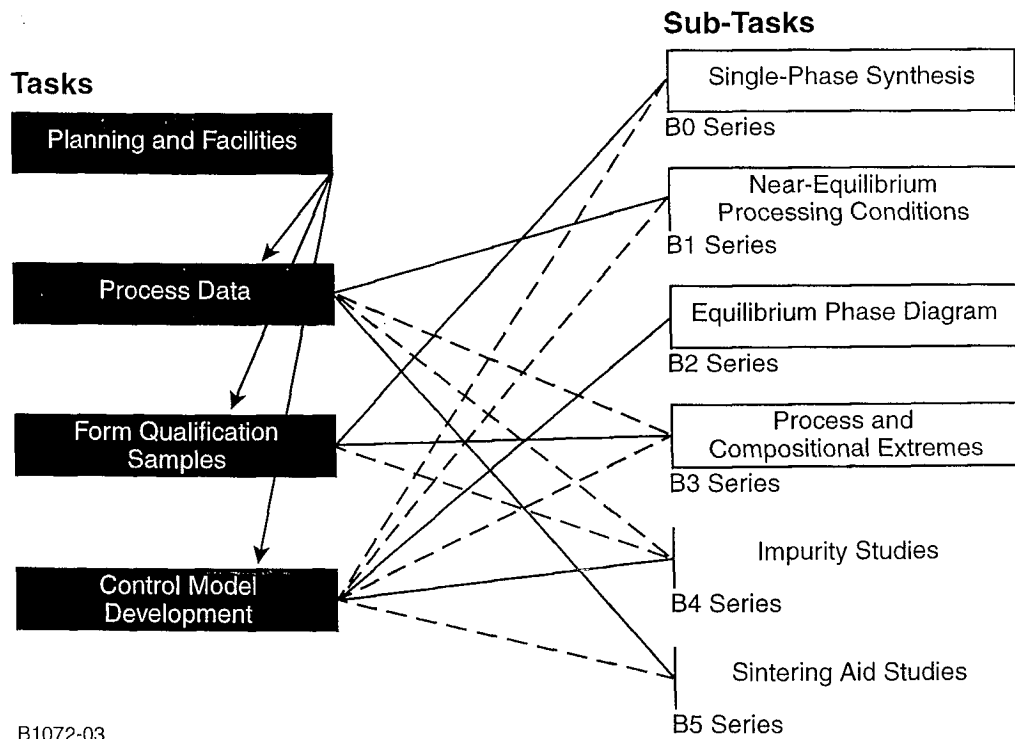
Figure 3.1 Linkages between tasks and sample test matrices.

Although a significant number of validation tests are being performed with plutonium, the majority of sample fabrications are performed with various non-radioactive surrogates. Surrogates are selected based on similarity of atomic size, melting point of the constituent oxide, and relative stability of the valence states. These data for plutonium, americium, and various surrogates are shown in **Table 3.2**. In the baseline ceramic, the best surrogate for plutonium is generally cerium. Its ionic size and the melting point of the constituent oxide are almost identical to plutonium.

If conditions in the sample preparation are moderately reducing, however, cerium can be a relatively poor surrogate for plutonium since it will generally convert to the trivalent ion whereas plutonium under the same conditions will generally remain as the tetravalent ion. Under more reducing conditions, thorium is believed to be a better surrogate for plutonium than cerium. Thorium is also preferred over cerium as a surrogate for plutonium in the "near-equilibrium" tests. Still, CeO_2 is observed to be much more reactive than PuO_2. ThO_2 has a considerably lower reactivity than CeO_2, and is much closer to that of PuO_2. For tests simulating americium-enriched material, neodymium is selected as the best surrogate. Based on the atomic size, melting points, and relative ionic stability, neodymium is expected to behave very similarly to americium in this ceramic.

To easily identify surrogates in a sample, the following nomenclature is used. A sample composed of all baseline elements and no surrogates is referred to as a hafnium-plutonium-uranium sample. If cerium is used as a surrogate for plutonium, the sample is referred to as a hafnium-cerium-uranium sample. Likewise, if thorium is used as a surrogate for plutonium, the sample is referred to as a hafnium-thorium-uranium sample. A sample where cerium is used as a surrogate for plutonium and uranium is referred to as a hafnium-cerium-cerium sample. If zirconium is used instead of hafnium, the same sample is a zirconium-cerium-cerium sample.

3.2.1 The A Series

There are 10 sample compositions in the A series. This series includes the baseline composition (A-0), six typical impurity feed compositions (A-1 to A-6) and three compositions with all the impurities: an average case (A-7), an extreme

Table 3.2 Surrogates for Plutonium and Americium.

Element	CN = 8 r^{4+}, (nm)	AnO_2 M.P. (°C)	An_2O_3/AnO_2 $p(O_2)^*$, (atm)
Ce	0.110	2600	2.3×10^{-11}
Th	0.119	3220	N/A
Pu	0.110	2425	2.5×10^{-18}

Element	CN = 8 r^{3+}, (nm)	An_2O_3 M.P. (°C)	An_2O_3/AnO_2 $p(O_2)^*$, (atm)
Nd	0.125	2315	$>6.9 \times 10^{-2}$
Am	0.123	>1200	2.1×10^2

$^*p(O_2)$ calculated at a temperature of 1350°C

case (A-8), and an intermediate case (A-9). For the most part, this series is complete. Some of the compositions continue to be fabricated to provide material for durability testing or to test the fabrication processes at full-scale.

3.2.2 The B Series

Whereas the smaller set of A series samples demonstrated that the ceramic form was suitable for the disposition of excess plutonium, the larger B series is aimed at understanding key parameters of the ceramic form, providing samples for durability testing, and providing data that will be needed to scale up and qualify the process. As shown in Figure 3.1, the B Series is divided into six subseries, each of which is discussed below.

3.2.2.1 Single-Phase Samples (B0 Series). These samples are needed for single-pass flow-through (SPFT) tests, enthalpy of formation measurements, entropy determinations, radiation damage studies, x-ray standards, and other select corrosion tests.

3.2.2.2 Near-Equilibrium Samples (B1 Series). These samples are needed to demonstrate that the product obtained by various "plant-like" processes is at or near chemical equilibrium.

3.2.2.3 Equilibrium Phase Diagrams (B2 Series). These samples are needed to define select phase equilibria in binary and ternary oxide systems. These phase equilibria will be essential in the developing the product control model.

3.2.2.4 Process and Compositional Extremes (B3 Series). These are samples prepared at process and compositional extremes. They are needed for durability and NDE testing. Some are needed for radiation damage studies.

3.2.2.5 Impurity Effects (B4 Series). These samples, the largest of the B series, are needed to determine feed specifications for the form and to develop the preliminary product control model. The B4 series is divided into three subseries as follows:

- *Impurity Saturation (B4-S)*. These samples are needed to determine which secondary phases form when saturated with specific impurities. This work is being performed primarily at LLNL.

- *Impurity Equivalence (B4-E)*. These samples are needed to determine which impurities are similar enough in behavior that they can be grouped together. This work is being performed primarily at ANSTO.

- *Impurity Volatility (B4-V)*. These samples are needed to determine the effect of volatile impurities on the product density. This work is being performed primarily at SRS.

3.2.2.6 Sintering Aid Studies (B5 Series). A sintering aid may be needed to increase the product density or to make product densities more uniform from sample to sample. These samples are needed to determine which impurities act most effectively as sintering aids.

In addition to the above samples, various samples are prepared on an as-needed basis to address various technical issues as they arise.

The B Series samples discussed above are summarized in **Table 3.3**. The table shows the sites fabricating, testing, or characterizing each samples; the total number of sample series; and the approximate fraction of completion for each series.

3.2.3 The C Series

The C series will be designed to define, test, refine, and validate the preliminary product control model. The samples in this series are not yet defined. However, the series will be a statistically designed test matrix that will likely involve several hundred samples. Sample fabrication will begin early in FY00. Once the tests in this series have been completed, the form development effort will be complete.

Table 3.3 Summary of the B Sample Test Matrices.

Series	I.D.	Sites Involved	Number*	Percent Complete
Single-Phase Synthesis	B0	ANL, ANSTO, LLNL, PNNL, SRS, and UCD	26 samples	50
Near-Equilibrium Processing Conditions	B1	ANSTO and LLNL	22 compositions	35
Equilibrium Phase Diagram	B2	ANSTO and LLNL	16 series	25
Process and Compositional Extremes	B3	ANL, LLNL, PNNL, and SRS	20 compositions	45
Impurity Studies	B4	ANSTO, LLNL, and SRS	53 series	60
Impurity Saturation	B4-S	LLNL	35 series	65
Impurity Equivalence	B4-E	ANSTO	12 series	50
Impurity Volatility	B4-V	SRS	6 series	60
Sintering Aid Studies	B5	LLNL and SRS	10 series	80

*Normally between two and twelve samples are made for each composition and between two and twelve compositions are made for each series.

4. Immobilization Form Specifications

4.1 Baseline Formulation

4.1.1 Composition

The baseline formulation is based upon the following target mineralogy and phase composition:

95.0 wt % pyrochlore ($Ca_{0.89}Gd_{0.22}Hf_{0.23}U_{0.44}Pu_{0.22}Ti_2O_7$)

4.0 wt % rutile (TiO_2)

1.0 wt % hafnia (HfO_2)

This target yields the overall baseline input composition (given in **Table 4.1**). This formulation is the baseline formulation. Note that up to about 3 wt% total of sintering aids may be added, if needed. If so, they will be specified after the fabrication process is finalized.

Table 4.1 The Overall Input Composition of the Baseline Ceramic.

Oxide	Baseline (wt%)	Low-Pu Alternative (wt%)	High-Pu Alternative (wt%)
CaO	9.952	9.488	9.950
HfO_2	10.653	11.100	10.651
UO_2	23.690	22.721	18.587
PuO_2	11.892	11.338	17.007
Gd_2O_3	7.951	7.580	7.949
TiO_2	35.862	37.773	35.856
Pu	10.488	10.000	15.000

Notes

Baseline. The baseline composition is to be used for immobilization of excess plutonium in a ceramic matrix. This is the baseline composition selected by the Form Development team.

Low-Plutonium Alternative (#1). If safeguards and security requirements at DWPF are such that the form must have 10 wt% plutonium or less in the product, the low-plutonium alternate can be used. The composition does not adversely impact repository licensing or design of the immobilization plant. Note, however, that the number of canisters produced will be increased by about 5%. In the low-plutonium alternate, the quantity of hafnium-substituted rutile is increased by roughly 5 wt%. The increase in rutile content lowers the plutonium content without changing the phase mineralogy. The extra rutile in this formulation will also give the formulation more flexibility to accommodate impurities in the plutonium feed streams.

High-Plutonium Alternative (#2). If circumstances arise such that the ceramic immobilization plant will immobilize the entire 50 metric tonnes of excess plutonium, a higher plutonium loading would be cost-effective and would not adversely affect plant design. The plutonium loading in the high-plutonium alternative is about 43% greater than in the baseline. Note that uranium and plutonium can be substituted in the formulation without significantly affecting the mineralogy of the product form. Note also that the plutonium feed specifications are dependent upon the plutonium concentration in the form (see Section 4.1.2 below).

In addition to the baseline formulation, the following two variants are also given. Each addresses specific programmatic requirements that may be desirable in the future.

1. Plutonium-loading may be dropped to 10 wt% to meet safeguards and security requirements at the Defense Waste Processing Facility (DWPF). This formulation is identified as the low-plutonium alternative in Table 4.1.

2. Plutonium-loading may be increased to 15 wt% if immobilization is selected as the means of dispositioning the entire 50 metric tonnes of excess plutonium. This formulation is identified as the high-plutonium alternative in Table 4.1.

The low-plutonium alternative composition (#1) is calculated by adding hafnium-substituted rutile to the baseline target mineralogy and phase composition. To achieve a 10 wt% plutonium loading, the target then becomes

95.34 wt% baseline formulation

95.0 wt% pyrochlore ($Ca_{0.89}Gd_{0.22}Hf_{0.23}U_{0.44}Pu_{0.22}Ti_2O_7$)

4.0 wt% rutile (TiO_2)

1.0 wt% hafnia (HfO_2)

4.66 wt% hafnium-rutile ($Ti_{0.90}Hf_{0.09}U_{0.01}O_2$)

In general, adding hafnium-rutile ($Ti_{0.90}Hf_{0.09}U_{0.01}O_2$) to the baseline composition gives a formulation with lower plutonium loadings but the same product mineralogy. The net result will be to generate more hafnium-rutile in the product. The presence of additional rutile will in general increase the capability of the formulation to accommodate impurities.

The high-plutonium alternative (#2) is calculated by substituting plutonium for uranium in the baseline target mineralogy and phase compositions. To achieve a 15 wt% plutonium loading, the target then becomes

95.0 wt% pyrochlore ($Ca_{0.89}Gd_{0.22}Hf_{0.23}U_{0.345}Pu_{0.315}Ti_2O_7$)

4.0 wt% rutile (TiO_2)

1.0 wt% hafnia (HfO_2)

Except for criticality control concerns at higher plutonium loadings, the baseline formulation can also be freely modified by trading uranium for plutonium or plutonium for uranium to get lower or higher plutonium loadings. The phase equilibrium data currently available indicate that these modifications will not significantly affect the product mineralogy. Note, however, that higher plutonium loadings reduce the formulation's capacity to accommodate impurities (see Equation 4.1 in Section 4.1.2).

Although the baseline formulation is now set at a 10.5 wt% plutonium loading, a range of other formulations are acceptable (e.g., by adding hafnium-rutile or by exchanging uranium for plutonium or plutonium for uranium in the formulation) if there is a need to increase or decrease the plutonium loading in the immobilization form. In other words, the formulation does not have to be limited to the baseline, low-plutonium, or the high-plutonium cases if another plutonium

loading is needed. Note, however, that the maximum plutonium loading in the form is 31.4 wt% (corresponding to composition in which all the uranium has been replaced by plutonium).

4.1.2. Precursor and Actinide Feed Specifications

The input compositions for the ceramic precursors are given in **Table 4.2**. A vendor would likely prepare these precursors. These compositions would be part of the specification in procuring the precursor material from a vendor. In both cases, Precursor 1 is the primary precursor, which contains CaO. Precursor 2 is a make-up precursor to offset calcium (present as CaO, $CaCl_2$, or CaF_2) in the PuO_2 feed streams. In both cases, Precursor 2 does not contain any CaO.

All materials added to the immobilization process need to meet specifications regarding form, particle size, and purity. The recommended specifications for the oxides used to prepare the ceramic precursor are given in **Table 4.3**. If the precursor materials meet the specifications given and the precursor is prepared by the process described in Section 4.2.1 below, the precursor produced will be suitable for use in the PIP. For HfO_2 and Gd_2O_3, a potential supplier is also given as an example of where the product can be obtained.

Table 4.2 Precursor Feed Compositions.

| | Baseline and High-Pu Alternate | | Low-Pu Alternate | |
| | Precursor 1 | Precursor 2 | Precursor 1 | Precursor 2 |
Oxide	(wt%)	(wt%)	(wt%)	(wt%)
CaO	15.449	0.00	14.389	0.00
HfO_2	16.537	19.559	16.833	19.662
Gd_2O_3	12.343	14.598	11.495	13.427
TiO_2	55.671	65.843	57.283	66.911

Table 4.3 Feed Specifications for Precursor Preparation.

Oxide	Form	Particle Size	Purity	Potential Supplier
CaO	$Ca(OH)_2$ (or CaO)	−325 mesh	>99% <1% CO2	Not Important
HfO_2	HfO_2	Micron sized or −600 mesh	Hf+Zr >99.99% Hf > 95 %	Wah Chang (S-Grade)
Gd_2O_3	Gd_2O_3	−325 mesh	REE >99.99% Gd >95%	Pacific Industrial Development Corporation
TiO_2	TiO_2 (anatase)	Micron sized or −600 mesh	>99.95% <0.05% P	Not Important

The preliminary specifications for the actinide oxides are given in **Table 4.4**. If the actinide oxides meet the specifications given, an acceptable ceramic product can be obtained. For plutonium oxide, the specification is that which the oxide must meet after blending. For uranium oxide, a potential supplier is also given as an example of where the product can be obtained.

The impurity specifications for the PuO_2 feed after blending are given in **Table 4.5**. In an attempt to simplify the specifications, impurities with similar behavior in the ceramic product are grouped into the same category. The specifications are given in moles of impurity per mole of PuO_2. Moles are used in the specification rather than weight percents because the impurities substitute into lattice sites in the ceramic matrix on an atomic basis, not a weight basis. The specifications given in Table 4.5 are basically the same specifications as given previously,[18] but reformatted to allow for more specificity. For example, zirconolite stabilizers will have a specification on the total amount of zirconolite stabilizers as well as specifications on the amount of +2, +3, and +4 stabilizers. Data are still being accumulated to complete this table.

The original impurity specifications for the PuO_2 feeds were based largely on the results obtained for the plutonium test sample of intermediate composition containing all impurities (A-9). Note that nickel, which was originally counted separately, has now been grouped with the zirconolite stabilizers. Consequently, the specification has been changed from 0.75 to 0.85. In addition, the trivalent REEs have been grouped with the pyrochlore stabilizers.

The specification on calcium has been increased dramatically (from 0.25 to 4.0) because a second precursor blend with no CaO component now compensates for variations in the calcium content of the plutonium feed. Uncompensated impurities are impurities that are added to the formulation without adjusting the composition or quantity of the precursor. Compensated impurities are impurities that are added to the formulation with adjustments in the precursor composition or quantity. For this process, most impurities are uncompensated. The actinides and calcium are the only compensated impurities.

The PuO_2 feed impurity specifications in Table 4.5 are valid for the baseline formulation only. For the low-plutonium alternative and the high-plutonium alternative, the specifications must be modified by the following relationship:

$$\text{(new spec)} = \text{(original spec)} \times 10.5/\text{(Pu wt\% in new formulation)} \qquad (4.1)$$

Note that the feed specifications become more stringent for the high-plutonium alternative and less stringent for the low-plutonium alternative.

Table 4.4 Uranium and Plutonium Oxide Feed Specifications.

Oxide	Form	Particle Size	Purity	Potential Supplier
UO_2	UO_2 (or U_3O_8)	−100 mesh	> 99.99%	Cameco
PuO_2	PuO_2 with UO_2 or U_3O_8	−100 mesh	See Table 4.5	N/A

Table 4.5 Impurity Specifications for Plutonium Oxide Feed.

Phase Stabilized	Moles Impurity per Mole of PuO_2	Elements or Compounds
Uncompensated		
Volatiles		
Fluorides	----	MgF_2, CaF_2
Chlorides	----	NaCl, KCl, $MgCl_2$, $ZnCl_2$, $CaCl_2$
Oxides (Metal)	----	$NaO_{0.5}$, $KO_{0.5}$, $CuO_{0.5}$
Oxides (Non-metal)	----	CO_x, SO_x, NO_x
Subtotal	0.60	
Zirconolite		
Divalent Elements	----	Co, Fe, Mg, Ni, Zn
Trivalent Elements	----	Al, Cr, Ga,
Tetravalent Elements	----	Zr, Hf, Sn
Subtotal	0.85	
Pyrochore		
Trivalent Elements	1.40	Gd, La, Y, Am
Tetravalent Elements	----	Ce
Pentavalent Elements	----	Nb, Ta
Hexavalent Elements	----	Mo, W
Subtotal		
Si	0.30	Si
B	0.15	B
Subtotal	0.30	
Whitlockite/Monazite		
P	0.10	P
Subtotal	0.10	
Hollandite/BaTiO3		
Ba	0.45	Ba
Subtotal	0.45	
Total Uncompensated	**1.75**	
Compensated		
Pyrochlore		
U (depleted or natural)	2.0	^{238}U
Pu	1.0	Pu
Other Actinides	1.0	^{233}U, ^{235}U, Np, Am
Sub total	3.0	
Perovskite		
Ca	4.0	Ca
Sub total	4.0	
Total Compensated	**7.0**	

4.1.3. Product Mineralogy

The approximate phase abundances in the baseline product are given in **Table 4.6**. When impurities are present in the PuO_2 feed, the relative abundances of the minerals can vary substantially from that of the baseline. Within the A series samples (see Table A-1 in Appendix A), the range of observed mineral abundances varies approximately as given in Table 4.6. The acceptable range as currently proposed is also given in the table. Note that the acceptable range has not yet been finalized. The range could be expanded when more durability and process development data are available. Based on the durability and process data currently available, it is not likely that the acceptable range will be narrowed from that given here.

As indicated in Table 4.6, the ceramic product contains a mixture of three actinide-bearing minerals (pyrochlore, zirconolite, and brannerite), some rutile, and a trace amount of partially or unreacted actinide oxide. The primary actinide-bearing phases all have natural mineral analogs that have survived for geologic time periods, which suggests that they are suitable actinide host phases for geologic disposal. Depending upon the impurity loadings in the PuO_2 feed, a variety of other phases could be present in small amounts.

4.1.3.1 Pyrochlore. Pyrochlore has a cubic structure similar to fluorite. The empirical formula unit is given as $A_2B_2O_6X$. The space group symmetry is Fd3m and each unit cell contains eight formula units. The coordination numbers of the A and B sites are 8 and 6, respectively.[19] For the plutonium ceramic, the A site can be occupied by Ca^{+2}, Gd^{+3}, U^{+4}, Pu^{+4}, and Hf^{+4}. The B site is occupied by Ti^{+4}, and the X site is occupied by O^{-2}.

Pyrochlore is a relatively common mineral in nature. Natural pyrochlores are grouped into three varieties: pyrochlore (niobium-rich), microlite (tantalum-rich), and betafite (titanium- and uranium-rich).[20] Of the three varieties, betafite most closely matches the composition of the pyrochlore phase in the plutonium ceramic. Some alteration in natural betafites is observed due to loss of relatively soluble matrix species such as NaF, KF, and CaO, but actinides are effectively retained by most betafites for geologic time periods up to 1.4 billion years.[21] If sufficient alteration has occurred by depletion of the soluble matrix species, a second stage of alteration can begin in which up to 30% of the original amount of uranium is lost. A large fraction of this uranium is retained in nearby phases.

Table 4.6 Phase Abundance in Baseline and Product Extremes.

Mineralogy	Baseline (vol%)	Observed Range (vol%)	Acceptable Range (vol%)
Pyrochlore	80	62 – 90	>50
Brannerite	12	0 – 22	0 – 50
Zirconolite	0	0 – 25	0 – 50
Rutile	8	0 – 16	0 – 20
Actinide Oxide	0.5	0.04 – 0.6	0 – 1
Other Minor Phases	0	0 – 6	0 –10

Baseline: The observed mineral abundances in the baseline product without impurities.

Observed Range: The approximate observed range of mineral abundances in the product with various impurities.

Acceptable Range: The proposed range over which the product mineralogy will be controlled.

The nominal compositions of betafite[21-23] and the plutonium pyrochlore phases are shown in **Table 4.7**. Although the compositions are similar, there are some significant differences between the composition of the natural pyrochlores and the pyrochlores in the plutonium ceramic. Most notably, the natural pyrochlores have substantial amounts of niobium and/or tantalum, whereas the pyrochlores in the plutonium ceramic do not contain any of these elements. Natural pyrochlores also contain small but significant amounts of sodium, potassium, and fluoride ions. These ions are generally the first to be depleted in natural pyrochlores that have undergone geochemical alteration.

4.1.3.2 Zirconolite. Zirconolite has many polytypes (i.e., structural variants)[24, 25] The most common polytype is zirconolite-2M, which is also the polytype found in the plutonium ceramic. Zirconolite-2M has a monoclinic structure. Zirconolite-4M is sometimes found in the plutonium ceramic, but the other known polytypes (zirconolite-3O, zirconolite-3T, and zirconolite-6T) have not yet been observed in the plutonium ceramic. All of the zirconolite polytypes and the pyrochlore structure are closely related to each other by the stacking of a common fundamental unit of TiO_6 octahedra that forms a linked plane of hexagonal and triangular rings.[23, 25] The hexagonal rings are joined to form planar layers. The polytypes differ in the way the layers are stacked. The most symmetric stacking of layers forms pyrochlore. All of the other stacking arrangements produce various zirconolite polytypes.

The empirical formula unit is given as ABC_2O_7. The space group symmetry is C_2/c and each unit cell contains eight formula units. The coordination numbers

Table 4.7. Nominal Composition of Plutonium Ceramic and Natural Analog Phases.

Element	Pyrochlore Pu Ceramic (mole)	Pyrochlore Natural (mole)	Zirconolite Pu Ceramic (mole)	Zirconolite Natural (mole)	Brannerite Pu Ceramic (mole)	Brannerite Natural (mole)
Na,K		0.06				
Ca	0.905	0.41	0.741	0.74	0.071	0.24
Y, REE[a]	0.217	0.04	0.147	0.08	0.110	0.07
Th		0.02		0.10		0.04
U	0.432	0.50	0.133	0.02	0.534	0.56
Pu	0.237		0.116		0.212	
Zr, Hf[b]	0.265	0.002	0.839	1.01	0.135	
Mg, Mn, Fe		0.23		0.36		0.18
Al	0.037	0.05	0.181	0.04	0.050	0.02
Ti	1.905	1.33	1.842	1.38	1.888	1.69
Nb, Ta		1.29		0.25		
Pb		0.04		0.003		0.03
Si		0.02		0.001		0.15
F		0.12				
O (calc)	6.964	7.76	7.093	6.94	5.849	5.53

[a]For the Pu ceramic Y, REE is Gd only

[b]For the Pu ceramic Zr, Hf is Hf and for the natural minerals Zr, Hf is Zr with a trace of Hf.

of the A and B sites are 8 and 7, respectively. There are three different C sites: two have a coordination number of 6 and one has a coordination number of 5.[25] For the plutonium ceramic, the A site can be occupied by Ca^{+2}, Gd^{+3}, and Pu^{+3}. The B site can be occupied by Hf^{+4}, Gd^{+3}, U^{+4}, and Pu^{+4}, and the C sites are occupied by Ti^{+4}.

Zirconolite minerals are also found in nature. Natural zirconolites up to 650 million years old have been found. With the exception of metamictization, no alteration has been observed and the actinides and decay products were retained in the mineral.[26] The nominal compositions of natural zirconolite[26-28] and the plutonium zirconolite phases are shown in Table 4.7. For the most part, the compositions of the natural zirconolites and the zirconolites in the plutonium ceramic are comparable.

4.1.3.3 Brannerite. The empirical formula unit of brannerite is given as AB_2O_6. Brannerite has a monoclinic structure and a space group symmetry is C2/m. There are two formula units per unit cell. Coordination numbers of the A and B sites are both 6.[29] In the plutonium ceramic, the A site can be occupied by U^{+4}, Pu^{+4}, and lesser amounts of Hf^{+4} and Gd^{+3}. The B site is occupied by Ti^{+4}.

Brannerites are also found in nature. Natural brannerites have not been well studied, but preliminary data suggests that brannerites up to 800 million years old are often pristine and unaltered. When alteration is observed, however, uranium loss can be severe. The nominal compositions of natural brannerites[29-31] and the plutonium brannerite phases are shown in Table 4.7. For the most part, the compositions of the natural brannerites and the brannerites in the plutonium ceramic are comparable.

4.1.3.4 Rutile. The empirical formula unit of rutile is given as AO_2. Rutile has a tetragonal structure and a space group symmetry of $P4^2/mnm$. Each unit cell contains two formula units. In the plutonium ceramic, the A site can be occupied by Ti^{+4} and lesser amounts of Hf^{+4}. Rutile does not accommodate any plutonium or any significant amount of uranium into its structure.

4.1.3.5 Actinide Oxide. The actinide oxides have a cubic fluorite structure. The empirical formula unit of actinide oxide is AO^2. The space group symmetry is Fm-3m and each unit cell contains four formula units. The coordination number of the A site is 8. In the plutonium ceramic, the A site can be occupied by U^{+4} and Pu^{+4} and lesser amounts of Hf^{+4} and Gd^{+3}.

4.1.3.6 Other Minor Phases. Depending upon the impurities present in the PuO_2 feed, any of the following phases could be present in small amounts in the ceramic product:

- Glasses (calcium-aluminum-titanium-silicates)

- Hafnium Titanate ($HfTiO_4$)

- Hollandite ($BaAl_2Ti_6O_{16}$)

- Loveringite ($CaTi_{21}O_{38}$)

- Magnetoplumbite ($CaAl_{12}O_{19}$)

- Perovskite ($CaTiO_3$)

- Pseudobrookite (Al_2TiO_5) – Armalcolite (Mg_2TiO_5)

- Scheelite ($CaWO_4$) – Powellite ($CaMoO_4$)

- Ulvospinel ($TiFe_2O_4$) – Spinel ($MgAl_2O_4$)

- Whitlockite ($Ca_3(PO_4)_2$) – Monazite ($GdPO_4$).

Example end-member compositions of these minerals are given in parentheses. Of these phases, the most common in the plutonium ceramic are glasses, perovskites, and pseudobrookite-armalcolites.

4.1.3.7. Phase Relationships. The acceptable phase compositional range of the ceramic form is an important boundary yet to be finalized for the plutonium ceramic. The boundary given in Table 4.6 is depicted in the simplified ternary diagram in **Figure 4.1**. Note that the baseline ceramic has six oxide components. To reduce the six-variable system to three variables, the following assumptions are made:

- UO_2 and PuO_2 behave similarly enough that they can be treated as one oxide, AnO_2

- TiO_2 is always in excess so the TiO_2 activity is fixed at unity

- Gd_2O_3 is distributed relatively evenly among the actinide-bearing phases so it is proportioned out of the phase equilibria.

Each of these assumptions reduces the variables by one, thus resulting in a three-variable system that can be plotted on the ternary diagram shown in Figure 4.1. The Baseline Precursor 1 composition is at 22.2 mol% HfO_2, 77.8 mol% CaO, and 0 mol% AnO_2 in the figure. Addition of UO_2/PuO_2 moves the composition in a straight line toward AnO_2. The intersection across the green region is the acceptable compositional regime as it is currently defined. Thus, between about 30 to 50 mol% AnO_2 can be added to the baseline product and an acceptable product will be produced. These boundaries will be modified slightly by the addition of impurities.

To help ensure that the immobilized plutonium is not separated from the neutron absorbers over time in the repository, it is important that the most abundant plutonium-bearing phases also accommodate significant quantities of the neutron absorbers. Although not as critical, it is more defensible in the repository license application if the less abundant plutonium-bearing phases also accommodate significant quantities of neutron absorbers. For each mineral phase that has been observed in the plutonium ceramic, its ability to accommodate gadolinium, hafnium, uranium, or plutonium is summarized in **Table 4.8**. Data are given as mole percent of element in the each phase. (Note that for each phase, between 60 and 70 mol% is oxygen.) Except for the residual actinide oxide, all of the primary phases accommodate more neutron absorbers (gadolinium and hafnium) than plutonium. Most of the other minor phases also accommodate more neutron absorbers (gadolinium and hafnium) than plutonium. The exceptions are magnetoplumbite and whitlockite/monazite. Magnetoplumbite has

T = 1350°C

P1 = Precursor 1 (with Ca)
A-0 = Baseline Composition

B = Brannerite
H = HfTiO$_4$
Pe = Perovskite
Py = Pyrochlore
Z = Zirconolite
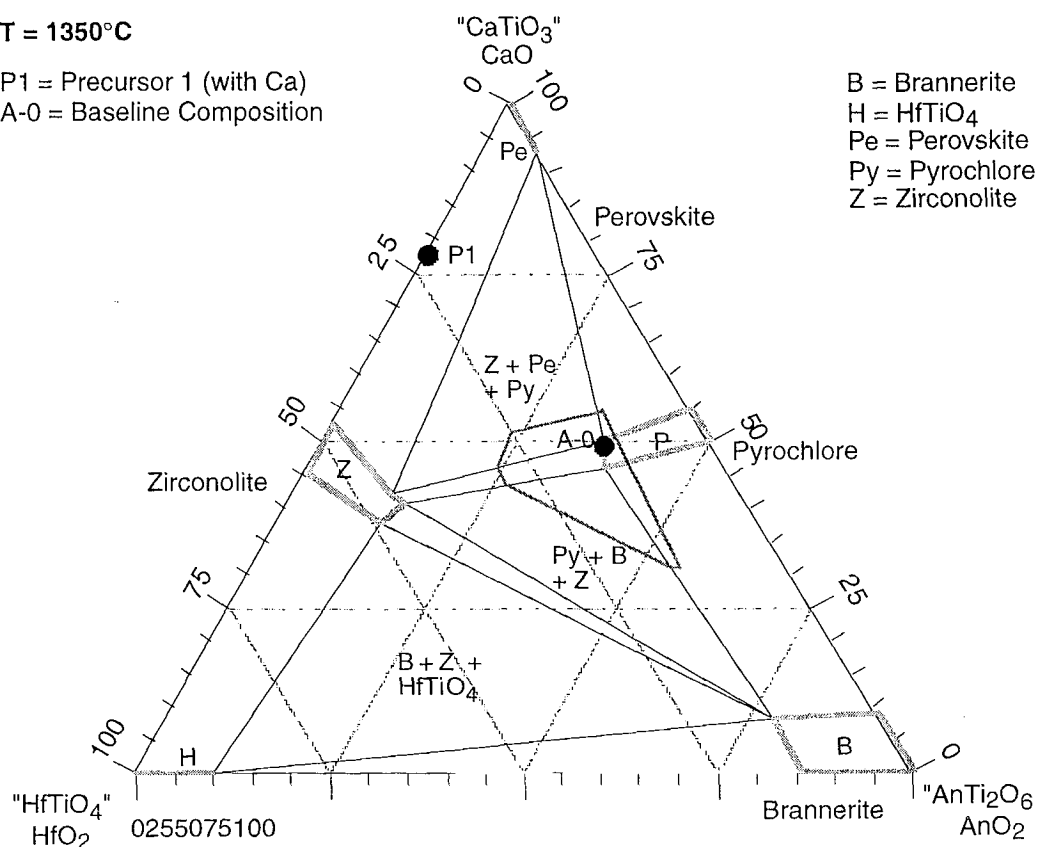
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Figure 4.1 Depiction of the processing regime.

Table 4.8 Actinides and Neutron Absorbers in the Primary Phases.

Primary Phases	Gd (mol%)	Hf (mol%)	U (mol%)	Pu (mol%)
Pyrochlore	2.0	1.8	3.7	2.1
Brannerite	1.4	1.2	5.7	2.4
Zirconolite-2M	1.4	6.4	1.4	1.0
Zirconolite-4M	1.3	4.6	2.0	1.4
Rutile	0.0	2.7	0.3	0.0
Actinide Oxide	1.6	1.0	<15	>13
Other Minor Phases				
Glass	0.4	0.2	0.7	0.3
Hafnium Titanate	~1.5	~15	~1.5	<0.1
Hollandite	0.2	0.7	0.3	0.2
Loveringite	<0.1	0.8	0.5	0.1
Magnetoplumbite	0.1	0.0	0.0	1.5
Perovskite	1.4	0.2	0.0	1.1
Pseudobrookite/Armalcolite	0.0	0.2	0.1	0.0
Scheelite/Powellite	<0.1	<0.1	<0.1	<0.1
Ulvospinel/Spinel	<0.1	<0.1	<0.1	<0.1
Whitlockite/Monazite	2.4	0.1	0.0	2.9

very little neutron absorbers and whitlockite/monazite has almost as much gadolinium as plutonium. Most phases that accommodate significant amounts of plutonium also accommodate significant amounts of uranium. The exceptions are magnetoplumbite, perovskite, and whitlockite/monazite, which accommodate plutonium but not uranium. These phases prefer trivalent actinides because the substitution occurs on the calcium site, and trivalent actinide ions are much closer in size to the Ca^{2+} ions than the tetravalent actinides. Substitution of plutonium into these phases is minimized by sintering under oxidizing conditions.

4.2 Baseline Fabrication Process

The baseline formulation could not be finalized without some definition of how the material is to be processed. In other words, the baseline formulation and the baseline fabrication process are not completely separable. As a result, the baseline fabrication process is an integral part of this report. The fabrication process is well developed, but most of the fabrication steps are not yet at a point to declare them as fully developed and issue final specifications. Even though the fabrication process is not yet final, the baseline formulation given above in Section 4.1 will remain valid as long as the following four criteria are met in the baseline fabrication process:

- The final fabrication process selected is not substantially different than the preliminary process described in this section

- The fabricated ceramic product is at or near equilibrium conditions

- The redox conditions during sintering are not altered (i.e., sintering atmosphere primarily, but could include lubricants or binders)

- The sintering temperature and time are not altered.

Significant changes in the fabrication process could affect feed specifications, e.g., form, particle size, and purity. The greater the deviation from equilibrium conditions in the as-fabricated ceramic product, the more the product properties depend on how the product was made. This creates more processing variables that affect product properties. If the as-fabricated ceramic product is at or near equilibrium conditions, only changes in feed composition, redox conditions during sintering, or sintering temperatures could significantly alter the product mineralogy.

The baseline fabrication process applies not only to the immobilization process, but also to the preparation of the precursor materials. The compositions of the precursors have been given in Section 4.1.1. The mixing recipes for precursor, uranium oxide, and plutonium oxide are given in Sections 4.3.1 and 4.3.2.

4.2.1 Ceramic Precursor Preparation

A commercial vendor will likely supply the oxide precursors to the Plutonium Immobilization Plant. The recommended precursor preparation process is shown in **Figure 4.2**. The recommended process consists of wet mixing/milling of the precursors, drying of the precursor slurry, and pulverization (i.e., size reduction) of the dried clumps as necessary. A final calcination step is performed to partially react the precursor materials and to remove residual materials that
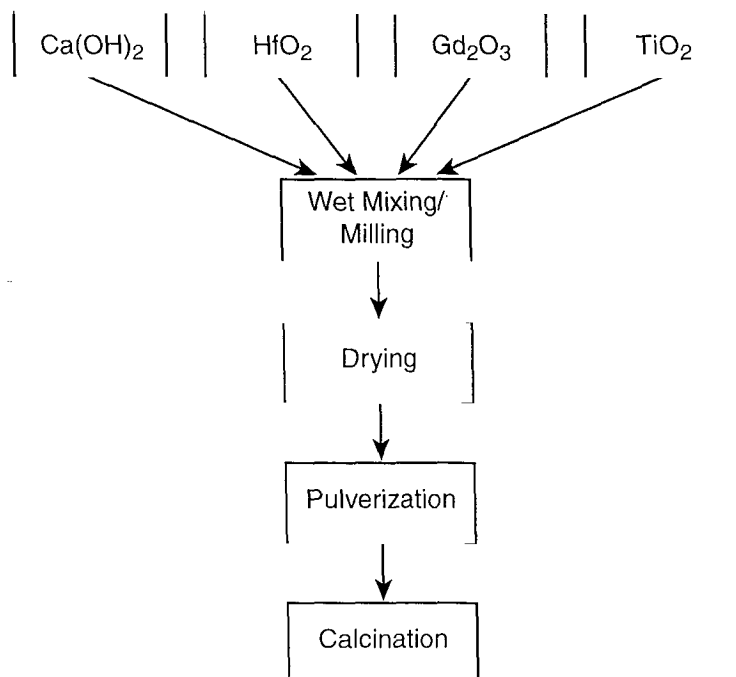
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Figure 4.2 Recommended process for preparing ceramic precursors.

will be volatile during the sintering process. Because a vendor will likely supply the precursor material, alternative preparation processes are acceptable as long as an acceptable product can be made. The process recommended here has been used successfully numerous times on full-scale fabrications of hafnium-cerium-cerium and hafnium-cerium-uranium formulations (i.e., ceramics in which cerium is used as an analog for plutonium or for both plutonium and uranium) and on several full-scale hafnium-plutonium-uranium fabrications.

4.2.1.1 Wet Mixing/Milling. In this step, the precursor feeds are weighed out and ball milled wet for a minimum of 1 hour. To minimize potentially incompatible contamination, the preference is to use a zirconia milling jar and zirconia grinding media.

4.2.1.2 Drying. In this step, the wet slurry is transferred to a tray and dried in an oven at about 110°C overnight (approximately 16 hours). Convection drying is preferred over vacuum drying.

4.2.1.3 Pulverization. After the drying step, a friable cake is formed. This cake must be size-reduced to a granular and flowable powder, which can be accomplished by using a flake breaker followed by a disk pulverizer.

4.2.1.4 Calcination. Calcination is used to decompose compounds and impurities that would release gas during the sintering process and to partially react the precursor material. Volatile impurities include but are not limited to nitrates and volatile salts. Partially reacting the precursor reduces the likelihood of crack formation during sintering. The key to calcination is to heat-treat the powdered

material at a temperature high enough that the gases are released, but low enough that most of the reactivity of the powder is retained. For this precursor composition, calcination between 600 and 750°C for 1 hour in air is recommended. The layer of powder should not be more than about 2 inches thick.

Processing of the precursors will be performed under appropriate quality assurance controls with limits placed on the acceptable impurities (see Table 4.5). After completion of all processing steps, the precursor materials will be packaged for shipment to the Plutonium Immobilization Plant. Packaging will require that no excess moisture or impurities enter the container.

4.2.2. Baseline Immobilization Process

The envisioned process flow diagram for the Plutonium Immobilization Plant is shown in **Figure 4.3**. The envisioned process has changed very little since the summer of 1997, but will continue to be investigated over the next few years to ensure that the processing parameters have been suitably optimized.

In summary, the process consists of dry milling the actinide oxides to under 20 μm, mixing/blending the milled actinides with commercially fabricated precursors, granulating (if needed) the milled/mixed powders, pressing the conditioned powders, and sintering the pressed pellets.

When the commercially supplied precursor is received at the Plutonium Immobilization Plant, it is anticipated that each lot of the vendor-supplied materials will be analyzed to ensure that the precursors are within acceptance specifications (see Section 4.1.2). The specifications have yet to be defined, but will likely cover the targeted chemical composition, mineral phases, impurity limits,
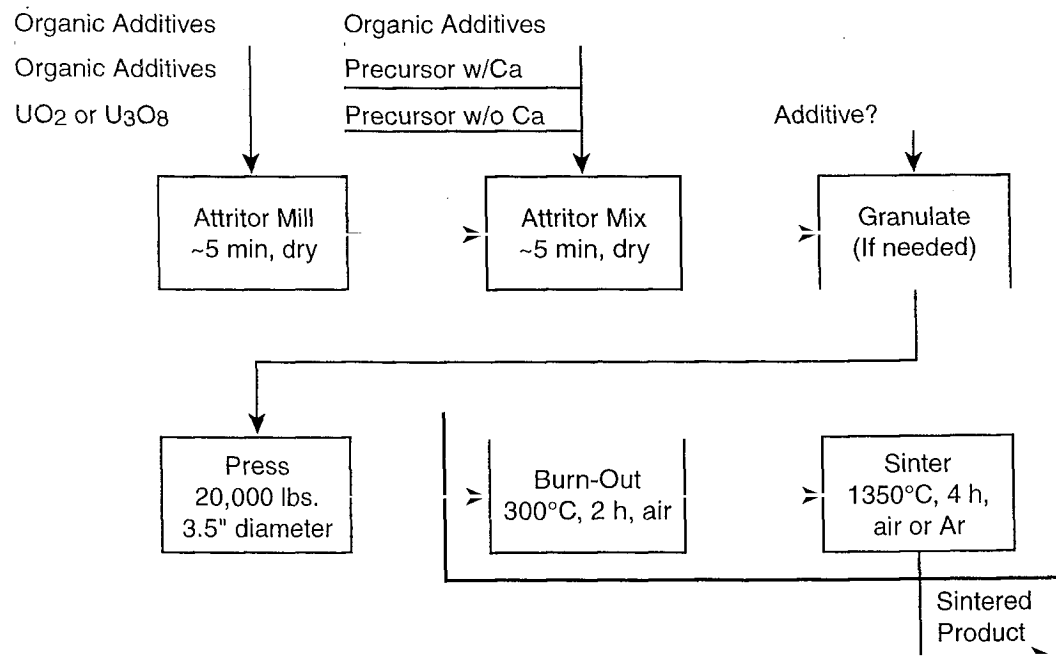
B1072-05

Figure 4.3 The ceramic immobilization process flow diagram attritor mill.

flowability constraints, moisture limits, and particle size of the precursor materials. Acceptance specifications will be similar to those currently in place for the glass frit used in the DWPF. It is anticipated that no batch of precursor material will be processed in the Plutonium Immobilization Plant without first undergoing acceptance testing to ensure that an acceptable product can be made.

The current process flow diagram is based on receiving PuO_2 from the plutonium conversion processes. The PuO_2 powder is expected to be almost entirely –150 mesh with reasonably well-known impurity contents. In order to minimize compositional variations and the effects of impurities on the plutonium ceramic form associated with the incoming PuO_2 feed stream, PuO_2 feed streams will be blended before milling occurs and before the PuO_2 is introduced into the plutonium immobilization line. The blended PuO_2 must meet the specifications in Table 4.5 before it can be immobilized. Out-of-specification material will be reblended.

Uranium oxide (depleted or natural) will also be added in the process to fabricate the plutonium ceramic form. The uranium oxide to be immobilized will most likely be from commercial fuel fabricators or from well-characterized excess DOE stock. The preferred form is UO_2, but U_3O_8 is also acceptable.

The milling operation is necessary to size-reduce the actinide oxide feed stream, as well as the recycle feed stream. The as-received actinides, which are expected to be nominally less than 150 µm, will require size reduction (to less than 20 µm) to assure adequate interaction during sintering. As for the recycle feed stream, the current equipment selected for crushing and grinding unacceptable pellets will nominally produce particles of approximately 100 µm, so further milling will be necessary to be able to accommodate this material into the form matrix.

The equipment selected for the milling operation is the attritor mill manufactured by Union Process. The attritor mill is best described as a stirred ball mill. A rotational shaft stirs the media at high speed, causing shearing and impact forces on the material, resulting in size reduction and dispersion. The high speed of the attritor mill imparts a large amount of energy to the feed powder. This high energy dramatically reduces the time required to mill—from hours to minutes. Another advantage of the attritor mill is that milling can be accomplished with a completely dry process. The attritor mill is manufactured in various sizes to accommodate different feed batch sizes, so scale-up of the mill should be easily accomplished.

During the normal operation of this equipment, a discharging aid is required. The use of the discharging aid is necessary to prevent excessive packing of the powders on the side of the mill and in the discharge valve. **Figure 4.4** shows the attritor mill discharging blended powders. Currently, 3 wt% polyolefin A-12 is being used as the baseline discharge aid. Polyolefin has been shown to work well as a discharge aid and has been shown to burn out cleanly from the pellets.

For accountability purposes, the input weight of actinide oxides to the attritor mill will be recorded and compared to the output weight during production. It is anticipated that there will be a holdup of a small amount of material. Once this heel has formed, the discharge from the mill has been shown to be approximately 100%.
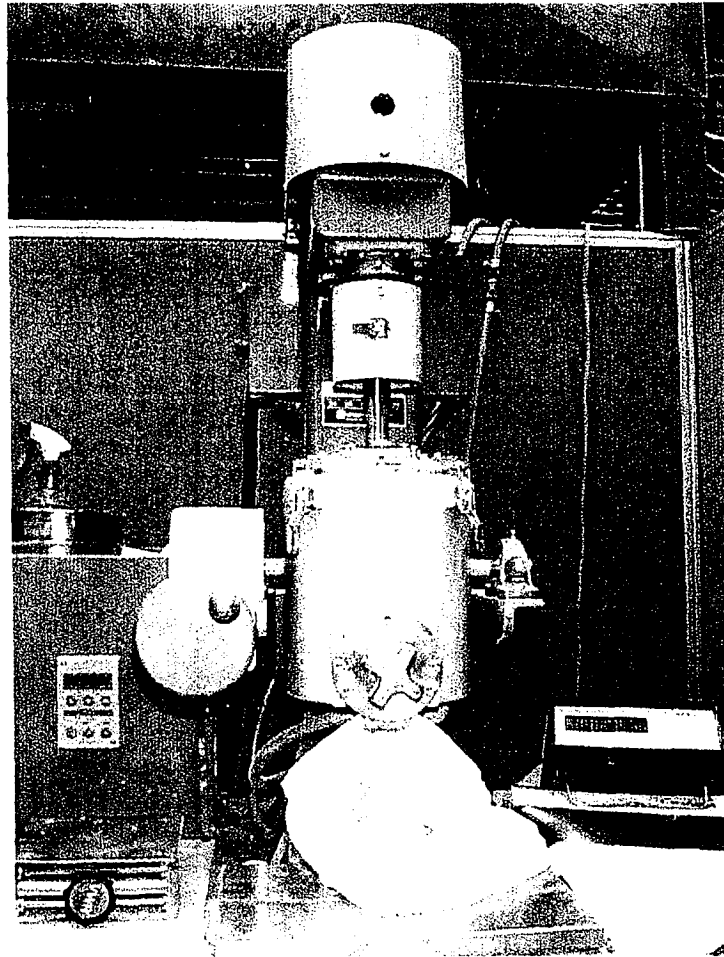
Figure 4.4 Attritor mill discharging blending ceramic precursor powders.

4.2.2.1 Attritor Mixing/Blending. The amount of precursors and actinide oxides to be blended will be determined by the equations given in Section 4.3.2. If the actinide oxide also meets the feed specifications given in Section 4.1.2, acceptable mineral phases will be produced. The acceptable mineral phases are given in Section 4.1.3.

A second, larger, attritor mill has been selected to perform ceramic precursor and actinide oxide micro-blending. Studies to date have shown that blending of precursors and actinide oxides on a micro-scale is necessary in order to produce dense and high-integrity pellets. Of the options tested (V-blender, wet ball-mill, dry ball-mill, and attritor), the attritor has been shown to be the best option for micro-scale blending. The high energy of the attritor provides excellent mixing with minimal time required.

It is hoped that the two precursor feeds and milled actinides can be fed to the blending attritor as three separate feed streams, so additional macro-scale blending equipment will not be necessary. Some of the testing results to date indicate that this may be possible. However, additional testing will be performed in the upcoming year on a larger attritor to see if omission of the macro-scale blending

equipment will be possible. If it is shown that this is not feasible, then the use of macro-scale blending equipment before the attritor mixing/blending step will be investigated.

Testing is also planned in the upcoming year to determine if the milling and mixing/blending processes can be combined into single process, thus eliminating the need for a dedicated milling attritor. The target amount of actinides with the corresponding amount of precursors would be added to the large blending attritor. In this attritor, the actinides would be milled and blended concurrently with the precursors. The elimination of an additional grinding step would also aid in keeping the actinide powders from becoming too small and hence more difficult to contain.

As with the milling operations, a discharge additive is also necessary during the blending operations to assist with feed recovery from the mill. Currently, the baseline additive for this step is also 3 wt% polyolefin (oxidized polyethylene), but studies in the upcoming year will also focus on optimizing this discharge additive.

As part of the process development program, the milled and blended powders will be analyzed to ensure that an acceptable composition has been produced and that sufficient homogeneity has been obtained. Before the blended powders are granulated, pressed and sintered, acceptability will have to be determined. The acceptability specifications will be defined as the program continues. It is uncertain at this time how often the feed will need to be analyzed in the plant for composition and homogeneity before the granulation, pressing, and sintering operations can be continued. In the plant, it is expected that this sort of analysis would be infrequent.

In addition to the precursors and the actinide oxides, a binder and/or lubricant will also likely be added to the blending attritor during the blending steps. The current baseline binder is polyethylene glycol 8K added at 5 wt% of the total feed. Optimization studies with different binders have been started and will be completed once the granulation equipment for the process is determined. Comparison studies with different equipment for powder conditioning for pressing will be performed in the upcoming year and binder testing will be finalized.

The current baseline process requires lubrication of the die set with 10 wt% oleic acid in acetone for each pellet that is pressed. However, to try to avoid external lubrication, studies in this upcoming year will look at using internal lubricants that can be mixed in with the powders.

4.2.2.2 Granulate. In order to condition the powders for pressing, it may be necessary to perform a granulation step on the blended powder. The purpose of the granulation step will be to help with powder flowability into the die set, minimize dusting of the powder, and assist with even filling of the die set. Investigation of several methods of granulation was begun this past year. These methods included tumbling (to help with powder agglomeration), roller compaction of the blended powders (to create harder and more consistent size granules), and fluidized bed preparation methods that sprayed the binder onto the granules. No definitive decisions were made on the optimal process: studies in the upcoming year will focus on defining this process step. Flowability of the

powder into the press is the key parameter and the requirements will be better-defined in the upcoming year.

4.2.2.3. Press. The current baseline process utilizes a 3.5-inch-diameter die for pressing the feed powders, which has been shown to produce the nominal sintered pellet target diameter, currently set at 2.625 inches (+0.125, -0.225). The die size is subject to change depending on the granulation process selected for the feed powder and the shrinkage behavior of the "green body" (i.e., pressed but not yet sintered pellet) during sintering.

The current press configuration is for double-action pressing, which will be tested extensively in the upcoming year. This double-action pressing should provide more even density distribution to the green pellet than the single-action pressing currently used. This is expected to minimize cracking that can occur during the sintering operation.

The milled, blended, and granulated powders will be pressed at the minimum pressure required to obtain high-density pellets with the appropriate mineral phases and minimal porosity. With the current powders being produced, the nominal pressure used is 20,000 pounds force or 2,000 psi pressing pressure to produce a 3.5-inch-diameter green pellet. A hold time of 10 seconds is currently used. Studies in the past have shown that the final density obtained is not dependent upon the pressing pressures unless pressures substantially less than 2,000 psi are used. However, different granulation methods being tested may require higher pressing pressures, so the pressing pressure used in the plant may be higher than 2,000 psi. The final pressure used will be defined in parameter optimization studies once the up-front processing and conditioning steps are better defined. These studies will also define the acceptable tolerances for production.

From the press, the green pellets will be transferred to the sintering furnaces using remote handling equipment. The envisioned plant design is for several furnaces to be available in the Plutonium Immobilization Plant so sintering of many pellets can be performed at one time.

The baseline sintering schedule and temperature has been defined to produce high density "pucks," while still allowing for some residual porosity in the sintered pellet. This residual porosity may be needed to reduce swelling and microcracking due to alpha-radiation damage of the ceramic over time. The theoretical density of the pellets has been defined as 5.98 g/cc, with acceptable densities currently defined as greater than 90% of theoretical.

4.2.2.4. Firing Schedule. The baseline sintering temperature is 1350°C for 4 hours in air. Heating and cooling rates are currently 5°C/minute with a slower initial rate and hold at 300° to burn out the binder. The sintering time and temperature will not change, but the ramp rates and binder burn-out schedule are still subject to change. Laser dilatometry studies are currently being performed to better refine this schedule. The sintering atmosphere is air, but argon could also be used after the binder is removed. The baseline firing schedule is depicted in **Figure 4.5**.

The parameters for the baseline firing schedule are given in **Table 4.9** and those for the baseline sintering schedule are given in **Table 4.10**. These processes are assumed to be performed one after the other to give the overall firing schedule given in Figure 4.5, but they could be accomplished in two steps with the same
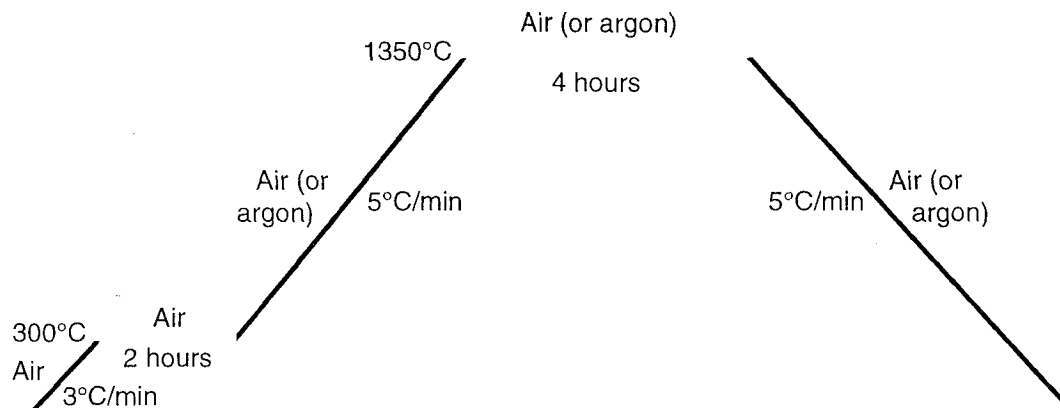
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Figure 4.5 The overall baseline firing schedule.

result. In the plant, it is currently assumed that, to reduce the cycle time, the sintered samples will be removed before they cool completely to room temperature.

4.3 Mixing Recipes

In the attritor mill, a relatively pure depleted or natural UO_2 feed will be blended with the relatively impure PuO_2 feed. The amount of UO_2 added to the PuO_2 will depend upon how much ^{238}U is already present in the PuO_2 feed. Depleted or natural UO_2 will be added to maintain a 2-to-1 molar ratio of uranium-to-plutonium. ThO_2 impurity in the PuO2 will be counted as $^{238}UO_2$ on a 1-to-1 molar basis. NpO_2, $^{233}UO_2$, $^{235}UO_2$, and $AmO_{1.5}$ will be counted as PuO_2 on a 1-to-1 molar basis. In the second attritor, the milled actinide oxides are blended with the two precursor feed streams. The relative amount of Precursor 2 is dependent upon the amount of calcium in the PuO_2 feed. The amount of Precursor 1 is dependent upon the amount of plutonium and the amount of calcium in the milled actinide oxide. The three parameters needed are defined as follows:

Table 4.9 Baseline Burn-out Schedule.

Segment	Start Temp. (°C)	End Temp. (°C)	Duration (min)	Atmosphere
1	30	300	90	Air
2	300	300	120	Air

Table 4.10 Baseline Sintering Schedule.

Segment	Start Temp. (°C)	End Temp. (°C)	Duration (min)	Atmosphere
1	300	1350	210	Air (or argon)
2	1350	1350	240	Air (or argon)
3	1350	300	210	Air (or argon)

X_{Ca}: Total mass of calcium in the PuO_2 feed

X_{NF}: Total mass of ^{238}U in the PuO_2 feed

X_F: Total mass of plutonium in the PuO_2 feed.

It is expected that the ^{235}U, neptunium, plutonium, and americium masses will be determined by material control and accountability (MC&A) equipment after blending. The thorium and ^{238}U contents will either be determined by MC&A after blending or will be known accurately enough from the original PuO_2 feed streams that were blended. The calcium content will need to be determined semi-quantitatively. Possibly it will be known well enough from the known or estimated composition in the original PuO_2 feed streams that were blended, but more likely it will need to be measured at least on a semi-routine basis. Note also that the amounts of all the other impurities do not affect the amounts of UO_2, Precursor 1, or Precursor 2 that will be added to the processes. The result is that the impurities are added over and above all of the other components and are not compensated for by varying the feed composition of any of the primary precursor constituents.

4.3.1 Attritor Mill Recipe

The amount of depleted or natural UO_2 that will added to the attritor mill is given by the equations in **Table 4.11**. X_F and X_{NF} are defined above. W_{UO2} is defined as follows:

W_{UO_2}: Mass of UO_2 (depleted or natural) added to the attritor mill.

If U_3O_8 is used instead of UO_2, multiply W_{UO_2} by 1.0395 to get $W_{U_3O_8}$.

Table 4.11 Mass of Depleted or Natural UO$_2$ Added to the Attritor Mill.

	Baseline	Low-Pu Alternative	High-Pu Alternative
W_{UO2}	= $2.25870X_F$ $- 1.13443X_{NF}$	= $2.27216X_F$ $- 1.13443X_{NF}$	= $1.23917X_F$ $- 1.13443X_{NF}$

4.3.2 Attritor Mixer/Blender Recipe

The amount of Precursor 1 and Precursor 2 that will be added to the attritor mixer/blender is given by the equations in **Table 4.12**. X_F and X_{NF} are defined above. $W_{Precursor\ 1}$ and $W_{Precursor\ 2}$ are defined as follows:

- $W_{Precursor\ 1}$: Mass of Precursor 1 (calcium-containing) to add to the attritor mixer/blender.

- $W_{Precursor\ 2}$: Mass of Precursor 2 (calcium-free) to add to the attritor mixer/blender.

Precursor 1 is the primary component added to the attritor mixer/blender. Precursor 2 does not contain any calcium and is used to offset calcium that is present in the PuO_2 feed stream.

Table 4.12 Mass of Precursor 1 and 2 Added to the Attritor Mixer/Blender.

	Baseline	Low-Pu Alternative	High-Pu Alternative
$W_{Precursor\ 1}$	$= 6.14187X_F$ $-9.05675X_{Ca}$	$=6.59428X_F$ $- 9.72426X_{Ca}$	$= 4.29385X_F$ $-9.05689X_{Ca}$
$W_{Precursor\ 2}$	$= 7.65757X_{Ca}$	$= 8.32507X_{Ca}$	$= 7.65770X_{Ca}$

4.3.3 Conversion Factors for Other Actinides

As mentioned above, ^{233}U, ^{235}U , neptunium, and americium are counted as plutonium in the formulation. The substitution is on an equimolar basis, not a weight basis. Since the molecular weights of ^{233}U, ^{235}U , neptunium, plutonium, and americium are relatively close, not much error is introduced by substituting on an equivalent mass basis, but the correct substitution accounting for molecular weight differences is given below:

$$X_F = X_{Pu} + (MW_{Pu}/MW_{233U})X_{233U} + (MW_{Pu}/MW_{235U})X_{235U} +$$

$$(MW_{Pu}/MW_{Np})X_{Np} + (MW_{Pu}/MW_{Am})X_{Am} \tag{4.2}$$

or

$$X_F = X_{Pu} + 1.02601X_{233U} + 1.01726X_{235U} + 1.00866X_{Np} + 0.99188X_{Am} \tag{4.3}$$

The same issue exists for substitution of thorium for ^{238}U. The correct substitution accounting for molecular weight differences is given below:

$$X_{NF} = X_{238U} + (MW_{238U}/MW_{Th})X_{Th} \tag{4.4}$$

or

$$X_{NF} = X_{238U} + 1.02591X_{Th} \tag{4.5}$$

For the above relationships the molecular weights are taken to be as follows:

- MW_{Th} = 232.038 g/mole

- MW_U = 238.029 g/mole

- MW_{233U} = 235.0439 g/mole

- MW_{235U} = 235.0439 g/mole

- MW_{238U} = 238.0508 g/mole

- MW_{Np} = 237.0480 g/mole

- MW_{Pu} = 239.1 g/mole

- MW_{Am} = 241.0567 g/mole.

4.3.4 Calculated Plutonium Ceramic Compositions

As an illustration of how the equations given in Tables 4.11 and 4.12 are used, they are applied to yield product compositions for the baseline formulation with four different PuO_2 feeds:

- Clean PuO_2 with no impurities

- An overall average feed for the 18-tonne immobilization case

- An average impure oxide case

- An extreme case of all the impurities.

The compositions of the various feeds have been given in Table 2.1. The product compositions calculated are given in **Table 4.13**. For simplicity, all the impurities have been grouped together. They are in the same ratio as given in Table 2.1. As expected, the composition calculated for clean PuO_2 matches the baseline composition shown in Table 4.1. Note that the compositions given are before sintering. Some of the impurities (e.g.., chlorine, fluorine, zinc) are volatilized at the sintering temperature and will be partially or completely volatilized, thus reducing slightly the total quantity of impurities in the sintered product.

Each of the compositions in Table 4.13 corresponds very closely to several of the compositions being tested in the sample test matrix. "Clean PuO_2" corresponds to A-0, "Average Feed" corresponds to B3-13, "Average Impure Oxide" corresponds to B3-17, and "Maximum All Feeds" corresponds to B3-19. To simplify sample fabrication on the B3-13, B3-17, and B3-19 compositions, [235]U, neptunium, and americium are counted as plutonium on a mole-per-mole basis and thorium is counted as 238U on a mole-per-mole basis.

Table 4.13 Product Compositions in Baseline Formulation.

Oxide	Clean PuO$_2$ (wt%)	Average Feed (wt%)	Average Impure Oxide (wt%)	Maximum All Feeds (wt%)
Primary Constituents				
CaO	9.952	9.374	9.008	7.889
HfO$_2$	10.653	10.271	9.643	8.509
UO$_2$	——	——	——	
ThO$_2$	0.000	0.000	0.000	0.001
UO$_2$	23.690	22.314	21.443	18.779
PuO$_2$	——			——
^{235}UO$_2$	0.000	0.000	0.000	0.000
NpO$_2$	0.000	0.113	0.000	0.317
PuO$_2$	11.892	10.614	10.764	8.716
Am$_2$O$_3$	0.000	0.463	0.000	0.383
Gd$_2$O$_3$	7.951	7.520	7.197	6.362
TiO$_2$	35.862	33.808	32.461	28.728
Impurities				
Total Impurities*	0.000	5.523	9.484	20.316

*Impurities are in the same abundance as shown in Table 2.1 except for carbon, which has been excluded.

5. The Path Forward

5.1 Preliminary, Final, and Recommended Specifications

The specifications given in this report are divided into three categories: preliminary, final, and recommended.

5.1.1 Preliminary Specifications

The preliminary specifications are still in development. However, it is assumed that when these specifications are finalized, they will not vary dramatically from those given in this report. The preliminary specifications given in this report are as follows:

- Baseline Formulation – Feed Specifications (Section 4.1.2)

- Baseline Formulation – Product Mineralogy (Section 4.1.3)

- Baseline Fabrication Process – Baseline Immobilization Process (Section 4.2.2).

5.1.2 Final Specifications

The final specifications will remain unchanged as long as there are no major changes in the plutonium disposition program assumptions and as long as the preliminary specifications still in development do not change dramatically from those given in this report. The final specifications given in this report are as follows:

- Baseline Formulation – Input Composition (Section 4.1.1)

- Mixing Recipes – Attritor Mill Recipe (Section 4.3.1)

- Mixing Recipes – Attritor Mixer/Blender Recipe (Section 4.3.2)

- Mixing Recipes – Conversion Factors for Other Actinides (Section 4.3.3).

5.1.3 Recommended Specifications

The recommended specification on the Baseline Fabrication Process – Ceramic Precursor Preparation (Section 4.2.1) is given as a reference to aid in the procurement specification.

5.2 Finalizing Preliminary Specifications

The specifications identified as preliminary will be finalized during the course of the D&T program. The milestones relevant to finalizing the preliminary specifications are given below. Milestones are taken from the Plutonium Immobilization Program D&T Plan dated August 1998.

5.2.1 The Baseline Formulation – Feed Specifications

The baseline formulation – feed specifications will be finalized in the form development task. The relevant milestones are:

- Provide Final Feed Specifications

- Provide Preliminary Product Control Model.

5.2.2 The Baseline Formulation – Product Mineralogy

The baseline formulation – product mineralogy will be finalized in the form development task. The relevant milestones are:

- Provide Form Summary Report for Repository License Application

- Provide Preliminary Product Control Model.

5.2.3 The Baseline Fabrication Process – Baseline Immobilization Process

The baseline fabrication process – baseline immobilization process specifications will be finalized as part of the process development task in first-stage immobilization.

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Appendix A
Detailed Test Matrices for Form Development

A.1 Series A Test Matrix

The detailed test matrix for the series A samples is given in **Table A-1**. Headings are defined as follows:

- *Subseries*. The ID for the sample, composition, or series. Each composition typically corresponds to between 2 and 12 samples and each series typically corresponds to between 2 and 12 compositions.

- *Sites*. The sites involved in the preparation of the sample, composition, or series. If this column is blank, the sample, composition, or series is very low priority at this time.

- *Composition*. A general description of the sample composition or range of compositions. Detailed compositions are given in Section A.3.

- *Plutonium Req.* The work with plutonium required in all samples, some samples, or no samples (for the sample, composition, or series).

- *Impurity Elements*. The description of the impurity elements added to the sample, composition, or series.

- *Impurity Amount*. The total weight percent of impurities or range of impurities added to the sample, composition, or series.

- *Fab*. The preparation status of the sample, composition, or series.

- *Dens*. The status of density measurements on fabricated samples.

- *Miner*. The status of sample characterization (e.g. SEM, x-ray diffraction).

- *Dur./Ther*. The status of durability testing or thermodynamic data measurements on the sample, composition, or series.

- *Addnl. Smpls*. The use of additional samples if needed after completion of testing on a sample, composition, or series.

A.2. Series B Test Matrices

The detailed test matrices for the B series follow. **Tables A-2** through **A-8** give progress against the test matrices. The headings on the test matrices are the same as those used for the A series (see Section A.1). Note that:

- Common Volatiles = B_2O_3, $CaCl_2$, CaF_2, KCl, PbO, $MgCl_2$, MgF_2, MoO_3, NaCl, WO_3, ZnO

- All Volatiles = Common Volatiles + K_2O, Na_2O, P_2O_5, PbO, and $ZnCl_2$

Table A-1 The Series A Sample Matrix.

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount	Fab.	Dens.	Miner.	Dur./ Ther.	Addnl. Smpls.
A-0	ANSTO PNNL, SRS, ANL	Baseline	S	None	0	Y	Y	Y	P	Y
A-1	SRS LLNL	Typical Impure Oxide	S	All	2.8%	Y	Y	Y	P	N
A-2	LLNL	ZPPR Fuel	S	MoO_3, Al_2O_3	0.6%	Y	Y	Y	P	N
A-3	ANSTO	Atypical Impure Metal	S	Ga_2O_3, MgO, Al_2O_3, Fe_2O_3, Ta_2O_5, NiO, WO_3	2.2%	Y	Y	Y	P	N
A-4	LLNL	Atypical Clean Metal	S	Ga_2O_3, ZnO, MgO	0.3%	Y	Y	Y	P	N
A-5	ANSTO	U/Pu Oxides	S	Al_2O_3, MgO, Fe_2O_3, MoO_3	1.0%	Y	Y	Y	P	N
A-6	SRS LLNL	Pu Alloys	S	Al_2O_3, MgO	1.2%	Y	Y	Y	P	N
A-7	LLNL ANSTO SRS	Average Impurity	S	All	1.5%	Y	Y	Y	P	N
A-8	LLNL ANSTO SRS	Extreme Oxide	S	All	13.0%	Y	Y	Y	P	N
A-9	LLNL ANSTO SRS ANL	Intermediate Impurity	S	All	5.1%	Y	Y	Y	P	Y

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-2 Series B0 Samples (Single Phases).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount	Fab.	Dens.	Miner.	Dur./Ther.	Addnl. Smpls.
B0-1	LLNL UCD ANSTO	$CaZrTi_2O_7$	N	None	N/A	Y	X	Y	Y	N
B0-2	LLNL ANSTO UCD	$CaHfTi_2O_7$	N	None	N/A	Y	X	Y	P	
B0-3	LLNL ANSTO	$CaCeTi_2O_7$	N	None	N/A	Y	X	Y	P	
B0-4	LLNL ANSTO	$CaPuTi_2O_7$	Y	None	N/A	P	X	P		
B0-5	ANSTO LLNL SRS	$CaUTi_2O_7$	N	None	N/A	Y	Y	Y		
B0-6	LLNL PNNL SRS ANSTO	$Gd_2Ti_2O_7$	N	None	N/A	Y	X	P	P	
B0-7	LLNL SRS ANSTO	$CeTi_2O_6$	N	None	N/A	Y	X	P		
B0-8	ANSTO LLNL	$PuTi_2O_6$	Y	None	N/A	P	X	P		
B0-9	ANSTO LLNL SRS	UTi2O6	N	None	N/A	P	X	P		
B0-10		CaTiO3	N	None	N/A	X				
B0-11	PNNL	Zirconolite ss (Ce)	N	None	N/A	Y	Y	Y	P	X
B0-12	PNNL	Pyrochlore ss (Ce)	N	None	N/A	Y	Y	Y	P	X
B0-13	PNNL	Brannerite ss (Ce)	N	None	N/A	Y	Y	P	P	X
B0-14	SRS, ANL	Glass (Ce)	N	None	N/A	Y	X	Y	X	X
B0-15	PNNL	Zirconolite ss (Pu)	Y	None	N/A	Y	Y	P		
B0-16	PNNL	Pyrochlore ss (Pu)	Y	None	N/A	P				
B0-17	PNNL	Brannerite ss (Pu)	Y	None	N/A	P				
B0-18	SRS, ANL	Glass (Pu)	Y	None	N/A	Y	X			
B0-19	PNNL	Brannerite ss (Th)	N	None	N/A	Y	Y	P		
B0-20		Perovskite ss (Pu)	Y	None	N/A	X				
B0-21		Perovskite ss (Ce)	N	None	N/A	X				
B0-22		Ca Phosphate (Pu)	Y	None	N/A	X				
B0-23		Ca Phosphate (Ce)	N	None	N/A	P				
B0-24	LLNL, ANL	Rutile ss	N	None	N/A	P				
B0-25	SRS	$CaHf-Zr-Ti_2O_7$	N	None	N/A	Y	X	Y	P	N
B0-26	UCD	Actinide oxide	Y	None	N/A	X				
B0-27	LLNL, SRS	Zirc w/2+ Imp (Ce)	N	2+ Impurities	max					
B0-28	LLNL, SRS	Zirc w/3+ Imp (Ce)	N	3+ Impurities	max					
B0-29	LLNL, SRS	Pyro w/5+ Imp (Ce)	N	5+ Impurities	max					
B0-30	LLNL, SRS	Pyro w/6+ Imp (Ce)	N	6+ Impurities	max					

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-3 Series B1 Samples (Near Equilibrium).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dens	Miner	Dur./Ther.	Addnl. Smpls.
B1-1	LLNL									
	ANSTO	A-0 (Pu)	Y	None	N/A	Y	Y	P		
B1-2	LLNL									
	ANSTO	A-0 (Th)	N	None	N/A	Y	Y	Y		
B1-3	LLNL	A-9 (Pu)	Y	None	N/A	Y	Y	P		
	ANSTO									
B1-4	LLNL	A-9 (Th)	N	None	N/A	Y	Y	Y		
	ANSTO									
B1-5	ANSTO	B3-1 (Pu)	Y	None	N/A	Y	Y	P		
B1-6	ANSTO	B3-1 (Th)	N	None	N/A	Y	Y	Y		
B1-7		B3-2 (Pu)	Y	None	N/A	X				
B1-8		B3-2 (Th)	N	None	N/A	X				
B1-9	ANSTO	B3-3 (Pu)	Y	None	N/A	Y				
B1-10	ANSTO	B3-3 (Th)	N	None	N/A	Y	Y	Y		
B1-11	ANSTO	B3-4 (Pu)	Y	None	N/A	Y				
B1-12	ANSTO	B3-4 (Th)	N	None	N/A	Y	Y	Y		
B1-13	ANSTO	B3-9 (Pu)	Y	None	N/A	!				
B1-14	ANSTO	B3-9 (Th)	N	None	N/A	Y	Y			
B1-15	ANSTO	B3-11 (Pu)	Y	None	N/A	!				
B1-16	ANSTO	B3-11 (Th)	N	None	N/A	Y	Y			
B1-17	LLNL	B3-13 (Pu)	Y	None	N/A	!				
B1-18	LLNL	B3-13 (Th)	N	None	N/A	!				
B1-19	LLNL	B3-17 (Pu)	Y	None	N/A	!				
B1-20	LLNL	B3-17 (Th)	N	None	N/A	!				
B1-21	LLNL	B3-19 (Pu)	Y	None	N/A	!				
B1-22	LLNL	B3-19 (Th)	N	None	N/A	!				

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-4 Series B2 Samples (Equilibrium Phase Diagram).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dur./	Dens	Miner Ther.	Addnl. Smpls.
B2-1	LLNL ANL	$CaTiO_3$-$CeTi_2O_6$-$HfTiO_4$	N	None	N/A	!				
B2-2		$CaTiO_3$-$ThTi_2O_6$-$HfTiO_4$	N	None	N/A	X?				
B2-3	LLNL ANL	$CaTiO_3$-UTi_2O_6-$HfTiO_4$	N	None	N/A	!				
B2-4	LLNL ANL	$CaTiO_3$-$PuTi_2O_6$-$HfTiO_4$	Y	None	N/A	!				
B2-5		$CaZrTi_2O_7$-$Gd_2Ti_2O_7$	N	None	N/A	X	N/A	N/A	N/A	N/A
B2-6	LLNL ANSTO	$CaHfTi_2O_7$-$Gd_2Ti_2O_7$	N	None	N/A	Y	X	P	X	Y
B2-7	LLNL ANSTO	$CaHfTi_2O_7$-$CaCeTi_2O_7$-$Gd_2Ti_2O_7$	N	None	N/A	!				
B2-8		$CaHfTi_2O_7$-$CaThTi_2O_7$-$Gd_2Ti_2O_7$	N	None	N/A	X?				
B2-9	LLNL ANSTO	$CaHfTi_2O_7$-$CaUTi_2O_7$-$Gd_2Ti_2O_7$	N	None	N/A	!				
B2-10	LLNL ANSTO	$CaHfTi_2O_7$-$CaPuTi_2O_7$-$Gd_2Ti_2O_7$	Y	None	N/A	!				
B2-11		CaO-ZrO_2-TiO_2	N	None	N/A	X	N/A	N/A	N/A	N/A
B2-12	ANSTO	CaO-HfO_2-TiO_2	N	None	N/A	!				
B2-13	LLNL ANSTO	CaO-CeO_2-TiO_2	N	None	N/A	!				
B2-14	LLNL	CaO-ThO_2-TiO_2	N	None	N/A	X?				
B2-15	ANSTO	CaO-UO_2-TiO_2	N	None	N/A	!				
B2-16	ANSTO	CaO-PuO_2-TiO_2	Y	None	N/A	!				

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-5 Series B3 Samples (Process and Compositional Extremes).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dens	Miner	Dur./Ther.	Addnl. Smpls.
B3-1		~95% Pyrochlore (Pu)	Y	None	N/A	X				
B3-2		Low in Gd and Hf (Pu)	Y	None	N/A	X				
B3-3	ANL PNNL SRS	Zirconolite-rich (Pu)	Y	None	N/A	Y	Y	P	Y	X
B3-4	ANL SRS	Brannerite-rich (Pu)	Y	None	N/A	Y	Y	P	Y	X
B3-5	LLNL	95% Pyrochlore (Ce)	N	None	N/A	Y	Y	Y	X	X
B3-6	LLNL	Low in Gd and Hf (Ce)	N	None	N/A	Y	Y	Y	X	X
B3-7	LLNL ANL SRS PNNL	Zirconolite-rich (Ce)	N	None	N/A	Y	Y	Y	P	X
B3-8	LLNL ANL SRS	Brannerite-rich (Ce)	N	None	N/A	Y	Y	Y	X	X
B3-9	ANL	~10% Perovskite (Pu)	Y	Excess CaO	~2%	!				
B3-10	ANL SRS	~10% Perovskite (Ce)	N	Excess CaO	~2%					
B3-11	ANL	~10% Phosphate (Pu)	Y	P_2O_5	~3.5%	!				
B3-12	ANL SRS	~10% Phosphate (Ce)	N	P_2O_5	~3.5%					
B3-13	LLNL ANL SRS	Average Impurity (Pu) !	Y	All	~6.6 %					
B3-14	LLNL ANL SRS	Average Impurity (Ce)	N	All	~6.7 %	!				
B3-15	LLNL	Am Enriched (Pu/Am)	Y	Am_2O_3	~0.6%	X				
B3-16	LLNL ANL SRS	Am Enriched (Ce/Nd)	N	Nd_2O_3	~0.4%	!				
B3-17	ANL	Avg. Impure Oxide (Pu)	Y	All	~10.6 %	!				
B3-18	ANL LLNL	Avg. Impure Oxide (Ce)	N	All	~10.9 %	!				
B3-19	ANL	Maximum Impurity (Pu)	Y	All	~25.0 %	!				
B3-20	ANL LLNL	Maximum Impurity (Ce)	N	All	~25.7 %	!				

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-6 Series B4-S Samples (Impurity Saturation).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount	Fab.	Dens	Mine	Dur./Ther.	Addnl Smpls.
B4-S1	LLNL	A-0	S	$AlO_{1.5}$	Saturated	Y	Y	Y	X	Y w/Pu
B4-S2	LLNL	A-0	Y	$AmO_{1.5}$	Saturated	X	N/A	N/A	N/A	N/A
B4-S3	LLNL	A-0	N	$BO_{1.5}$	Saturated	Y	Y	P		
B4-S4	LLNL	A-0	N	BaO	Saturated	Y	Y	P		
B4-S5	LLNL	A-0	S	CaO	Saturated	Y	X	Y	X	Y w/Pu
B4-S6	LLNL	A-0	N	CeO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S7	LLNL	A-0	N	$CrO_{1.5}$	Saturated	Y	Y	P		
B4-S8	LLNL	A-0	N	$CuO_{0.5}$	Saturated	Y	X			
B4-S9	LLNL	A-0	N	$FeO_{1.5}$	Saturated	Y	X	Y	X	X
B4-S10	LLNL	A-0	S	$GaO_{1.5}$	Saturated	Y	Y	P		
B4-S11	LLNL	A-0	N	$GdO_{1.5}$	Saturated	X	N/A	N/A	N/A	N/A
B4-S12	LLNL	A-0	N	HfO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S13	LLNL	A-0	N	$KO_{0.5}$	Saturated	!				
B4-S14	LLNL	A-0	N	$LaO_{1.5}$	Saturated	X	N/A	N/A	N/A	N/A
B4-S15	LLNL	A-0	S	MgO	Saturated	Y	X	Y	X	Y w/Pu
B4-S16	LLNL	A-0	N	$MnO_{1.5}$	Saturated	Y	X			
B4-S17	LLNL	A-0	N	MoO_{2+x}	Saturated	Y	Y	P		
B4-S18	LLNL	A-0	N	$NaO_{0.5}$	Saturated	Y	Y	P		
B4-S19	LLNL	A-0	N	$NbO_{2.5}$	Saturated	Y	Y	P		
B4-S20	LLNL	A-0	N	NiO	Saturated	Y	X			
B4-S21	LLNL	A-0	N	$NdO_{1.5}$	Saturated	X	N/A	N/A	N/A	N/A
B4-S22	LLNL	A-0	Y	NpO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S23	LLNL	A-0	S	$PO_{2.5}$	Saturated	Y	X	Y	X	Y w/Pu
B4-S24	LLNL	A-0	N	PbO	Saturated	!				
B4-S25	LLNL	A-0	S	SiO_2	Saturated	Y	Y	P		
B4-S26	LLNL	A-0	N	SnO_2	Saturated	!				
B4-S27	LLNL	A-0	N	$TaO_{2.5}$	Saturated	Y	Y	P		
B4-S28	LLNL	A-0	N	ThO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S29	LLNL	A-0	N	TiO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S30	LLNL	A-0	N	$VO_{1.5}$	Saturated	Y	Y	Y	X	X
B4-S31	LLNL	A-0	N	WO_{2+x}	Saturated	Y	Y	P		
B4-S32	LLNL	A-0	N	ZnO	Saturated	Y	X			
B4-S33	LLNL	A-0	N	ZrO_2	Saturated	X	N/A	N/A	N/A	N/A
B4-S34	LLNL									
	ANL	A-0	N	C	Saturated	Y	Y	Y	X	X
B4-S35	LLNL	A-0	N	CaF_2	Saturated	Y	Y	Y	X	X

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-7. Series B4-E Samples (Impurity Equivalence).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dens	Miner	Dur./Ther.	Addnl. Smpls.
B4-E1	ANSTO	A-0	S	+2	As Needed	Y	Y	Y		
B4-E2	ANSTO	A-0	S	+3	As Needed	Y	Y	Y		
B4-E3	ANSTO	A-0	S	+4	As Needed	Y	Y	Y		
B4-E4	ANSTO	A-0	S	+6	As Needed	Y	Y	Y		
B4-E5	ANSTO	A-0	S	+5	As Needed	Y	Y	Y		
B4-E6	ANSTO	A-0	S	+4 Actinde	As Needed	Y				
B4-E7	ANSTO	A-0	S	Variable	As Needed	P				
B4-E8	ANSTO	A-0	S	+3/+4= +2 /+5	As Needed	X				
B4-E9	ANSTO	A-0	S	+2/+4= +3/+3	As Needed	X				
B4-E10	ANSTO	A-0	S	+3/+4= +2/+5	As Needed	X				
B4-E11	ANSTO	A-0	S	+2/+2= +1/+3	As Needed	X				
B4-E12	ANSTO	A-0	S	+2/+4= +4/+2	As Needed	X				

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-8 Series B4-V Samples (Impurity Volatility).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dens	Miner	Dur./Ther.	Addnl. Smpls.
B4-V1	SRS	A-0	N	Common	Fixed (0.600)	Y	Y	Y	X	Y
B4-V2	SRS	B3-3/7	N	Common	Fixed (0.600)	Y	Y	Y	X	Y
B4-V3	SRS	B3-4/8	N	Common	Fixed (0.600)	Y	Y	Y	X	Y
B4-V4	SRS	A-0	S	All	Variable	X				
B4-V5	SRS	B3-3/7	S	All	Variable	X				
B4-V6	SRS	B3-4/8	S	All	Variable	X				

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Common Volatiles = B_2O_3, $CaCl_2$, CaF_2, KCl, PbO, $MgCl_2$, MgF_2, MoO_3, NaCl, WO_3, ZnO
All Volatiles = Common Volatiles + K_2O, Na_2O, P_2O_5, PbO, and $ZnCl_2$

A.3. Detailed Compositional Descriptions

Tables **A-9** through **A-14** give the detailed compositions of the various samples referred to in the A and B test series matrices.

Table A-9 Series B5 Samples (Sintering Aids).

Sub-Series	Site(s)	Composition	Pu Req.	Impurity Elements	Impurity Amount.	Fab.	Dens	Miner	Dur./ Ther.	Addnl. Smpls.
B5-1	LLNL									
	SRS	A-0	N	NaOH	<3%	Y	Y	P		
B5-2	LLNL									
	SRS	A-0	N	NaF	<3%	Y	Y	Y	X	X
B5-3	LLNL									
	SRS	A-0	N	Na_2SO_4	<3%	Y	Y	P		
B5-4	LLNL									
	SRS	A-0	N	BaO	<3%	Y	Y	P		
B5-5	LLNL									
	SRS	A-0	N	CaF_2	<3%	X?				
B5-6	LLNL									
	SRS	A-0	N	Al_2O_3	<3%	Y	Y	Y	X	X
B5-7	LLNL									
	SRS	A-0	N	B_2O_3	<3%	Y	Y	Y	X	X
B5-8	LLNL									
	SRS	A-0	N	P_2O_5	<3%	Y	Y	Y	X	X
B5-9	LLNL									
	SRS	A-0	N	SiO_2	<3%	Y	Y	Y	X	X
B5-10	LLNL									
	SRS	A-0	S	Mix	<3%	X	N/A	N/A	N/A	N/A
B5-11	LLNL									
	SRS	A-0	N	Na_2CO_3	<3%	Y	Y	P		

Y = Yes, N = No, S = Some, P = Partial Completion or In Progress, ! = Needed, X = Not Needed or Do Later

Table A-10 Detailed Compositions for A Series Samples.

	A-0 (wt%)	A-1 (wt%)	A-2 (wt%)	A-3 (wt%)	A-4 (wt%)	A-5 (wt%)	A-6 (wt%)	A-7 (wt%)	A-8 (wt%)	A-9 (wt%)
Base Feed Materials										
CaO	9.95	9.67	9.89	9.73	9.92	9.85	9.83	9.80	8.65	9.44
TiO_2	35.87	34.88	35.64	35.08	35.77	35.50	35.43	35.34	31.20	34.04
HfO_2	10.65	10.35	10.58	10.41	10.62	10.54	10.52	10.49	9.26	10.11
Gd_2O_3	7.95	7.73	7.90	7.77	7.93	7.87	7.85	7.83	6.91	7.54
UO_2	23.69	23.03	23.54	23.17	23.63	23.45	23.4	23.34	20.60	22.48
PuO_2	11.89	11.56	11.81	11.63	11.86	11.77	11.75	11.71	10.34	11.28
Impurities										
Al_2O_3		0.63	0.20	0.22		0.11	1.04	0.32	1.59	0.50
MgO		0.19		0.23	0.02	0.46	0.18	0.13	0.87	0.44
$CaCl_2$		0.37						0.16	2.19	0.66
Ga_2O_3				1.27	0.14			0.14		0.57
Fe_2O_3		0.17		0.14		0.16		0.08	0.50	0.15
Cr_2O_3		0.04		0.02				0.02	0.13	0.08
NiO		0.08		0.09				0.04	0.33	0.13
CaF_2		0.21						0.12	1.30	0.44
K_2O		0.15		0.04				0.07	1.05	0.32
Na_2O		0.16						0.06	0.47	0.14
MoO_2		0.05	0.44			0.30		0.11	0.47	0.28
SiO_2		0.51						0.19	1.50	0.46
Ta_2O_5		0.05		0.15				0.06	0.64	0.19
B_2O_3		0.04							0.34	0.17
WO_2		0.14		0.06					1.64	0.49
ZnO					0.11			0.01		0.07
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table A-11 Detailed Compositions for B0 Series Samples (B0-19 to B0-23).

	BO-11 (wt %) zirconolite ss (Ce)	BO-12 (wt %) pyrochlore ss (Ce)	BO-13 (wt %) brannerite ss (Ce)	BO-14 (wt %) glass (Ce)	BO-15 (wt %) zirconolite ss (Pu)	BO-16 (wt %) pyrochlore ss (Pu)	BO-17 (wt %) brannerite ss (Pu)	BO-18 (wt %) glass (Pu)
Base Feed Materials								
CaO	10.481	10.393		13.20	10.198	9.942		13.08
TiO_2	34.533	38.495	42.197	8.15	33.601	36.825	37.758	8.08
HfO_2	44.259	10.080	2.779	1.38	43.064	9.643	2.487	1.37
Gd_2O_3	2.117	8.303	2.393	1.07	2.060	7.943	2.141	1.06
UO_2	1.892	24.739	32.084	2.69	1.841	23.666	28.709	2.67
PuO_2					7.396	11.880	28.815	2.43
ThO_2								
CeO_2	4.826	7.885	20.445	1.56				
Impurities								
Al_2O_3	1.786			19.67	1.738			19.49
MgO				1.32				1.31
Ga_2O_3				2.57				2.55
Fe_2O_3				0.45				0.45
K_2O				0.66				0.65
Na_2O				3.37				3.34
MoO_2	0.105	0.105	0.102	0.44	0.102	0.100	0.091	0.44
P_2O_5				2.69				2.67
SiO_2				35.30				34.99
B_2O_3				5.47				5.42
Total	100.00	100.00	100.00	99.99	100.00	100.00	100.00	100.00

Table A-12 Detailed Compositions for B0 Series Samples (B0-19 to B0-23).

	BO-19 (wt%) brannerite ss (Th)	BO-20 (wt%) perovskite ss (Pu)	BO-21 (wt%) perovskite ss (Ce)	BO-22 (wt%) Ca-phosphate (Pu)	BO-23 (wt%) Ca-phosphate (Ce)
Base Feed Materials					
CaO		30.693	31.819	26.515	28.973
TiO2	38.043	51.129	53.004	2.072	2.264
HfO2	2.506	1.442	1.495	1.004	1.097
Gd2O3	2.157	6.873	7.125	13.465	14.713
UO2	28.926	0.173	0.179	0.332	0.362
PuO2		9.690		23.227	
ThO2	28.276				
CeO2			6.378		16.112
Impurities					
MoO2	0.092				
P2O5				33.386	36.480
Total	100.00	100.00	100.00	100.00	100.00

Table A-13 Detailed Compositions for B3 Series Samples (B3-1 to B3-8).

	B3-1 (wt%) 95% (Pu) pyrochlore	B3-2 (wt%) Low in Gd & Hf (Pu)	B3-3 (wt%) Zirconolite rich (Pu)	B3-4 (wt%) Brannerite rich (Pu)	B3-5 (wt%) 95% (Ce) pyrochlore	B3-6 (wt%) Low in Gd & Hf (Ce)	B3-7 (wt%) Zirconolite rich (Ce)	B3-8 (wt%) Brannerite rich (Ce)
Base Feed Materials								
CaO	9.999	9.654	9.236	5.837	10.484	10.267	9.570	6.127
TiO_2	34.530	33.472	33.846	36.989	36.204	35.596	35.072	38.829
HfO_2	11.933	6.268	24.209	9.920	12.511	6.666	25.086	10.413
Gd_2O_3	7.749	3.758	6.600	6.320	8.125	3.996	6.839	6.634
UO_2	23.129	30.502	15.404	27.956	24.250	32.438	15.962	29.346
PuO_2	12.659	16.347	9.573	12.978				
CeO_2					8.427	11.038	6.298	8.650
Impurities								
Al_2O_3			1.132				1.173	
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Table A-14 Detailed Compositions for B3 Series Samples (B3-9 to B3-12, B3-15, & B3-16).

	B3-9 (wt%) 10% (Pu) perovskite	B3-10 (wt%) 10% (Ce) perovskite	B3-11 (wt%) 10% (Pu) phosphate	B3-12 (wt%) 10% (Pu) phosphate	B3-15 (wt%) Am enrich. (Pu/Am)	B3-16 (wt%) Am enrich. (Ce/Nd)
Base Feed Materials						
CaO	12.068	12.639	11.608	12.188	9.952	10.427
TiO_2	36.19	37.901	32.483	34.105	35.862	37.573
HfO_2	10.884	11.399	9.688	10.172	10.653	11.161
Gd_2O_3	7.661	8.023	8.502	8.927	7.951	8.330
UO_2	20.833	21.818	21.354	22.420	23.113	24.216
PuO_2	12.362		13.026		11.892	
CeO_2		8.22		8.683		7.910
Am_2O_3					0.577	
Nd_2O_3						0.383
Impurities						
P_2O_5			3.339	3.506		
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Table A-15 Detailed Compositions for B3 Series Samples (B3-13, B3-14, & B3-17 to B3-20).

	B3-13 (wt%) Average Imp. (Pu)	B3-14 (wt%) Average Imp. (Ce)	B3-17 (wt%) Avg. Imp. Oxide (Pu)	B3-18 (wt%) Avg. Imp. Oxide (Ce)	B3-19 (wt%) Maximum Oxide (Pu)	B3-20 (wt%) Maximum Oxide (Ce)
Base Feed Materials						
CaO	8.300	8.654	7.920	8.244	3.185	3.298
TiO_2	33.804	35.246	32.461	33.789	28.725	29.749
HfO_2	10.270	10.708	9.643	10.037	8.508	8.812
Gd_2O_3	7.519	7.840	7.197	7.491	6.361	6.588
UO_2	22.312	23.263	21.443	22.320	18.777	19.446
PuO_2	11.200		10.764		9.426	
CeO_2	0.184	7.606	0.144	7.264	0.231	6.437
Impurities						
Al_2O_3	0.723	0.753	2.437	2.537	1.307	1.354
B_2O_3	0.101	0.106	0.176	0.183	0.216	0.224
BaO	0.143	0.149	0.122	0.127	0.436	0.451
$CaCl_2$	0.667	0.695	1.114	1.159	1.687	1.747
Cr_2O_3	0.050	0.052	0.151	0.157	0.174	0.181
Cu_2O	0.117	0.122	0.000	0.000	0.262	0.271
CaF_2	1.025	1.068	0.731	0.761	5.361	5.552
FeO	0.187	0.195	0.513	0.534	0.635	0.657
Ga_2O_3	0.387	0.404	0.000	0.000	1.119	1.159
K_2O	0.225	0.234	0.962	1.002	0.834	0.864
La_2O_3	0.017	0.018	0.024	0.025	0.175	0.181
MgO	0.433	0.452	0.979	1.019	3.249	3.365
MnO	0.000	0.000	0.000	0.000	0.008	0.008
MoO_2	0.161	0.168	0.175	0.183	0.278	0.288
Na_2O	0.232	0.242	0.388	0.403	0.277	0.287
NiO	0.086	0.090	0.292	0.304	0.296	0.307
Nd_2O_3	0.291	0.303	0.000	0.000	1.278	1.323
P_2O_5	0.006	0.006	0.000	0.000	0.138	0.143
PbO	0.516	0.538	0.000	0.000	1.000	1.035
SiO_2	0.880	0.918	2.139	2.227	4.918	5.093
SnO_2	0.006	0.006	0.000	0.000	0.025	0.026
Ta_2O_5	0.080	0.083	0.224	0.233	0.646	0.669
WO_2	0.017	0.018	0.000	0.000	0.221	0.229
ZnO	0.060	0.063	0.000	0.000	0.244	0.253
ZrO_2	0.000	0.000	0.000	0.000	0.002	0.002
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

Appendix B
List of Acronyms

ANL	Argonne National Laboratory
ANSTO	the Australian Nuclear Science Technology Organization
BEI	backscatter electron image
BNFL	British Nuclear Fuels Limited
DOE	Department of Energy
DOE-DP	Department of Energy Offices of Defense Programs
DOE-EM	Department of Energy Environmental Management
DOE-MD	Department of Energy Materials Disposition Program
DOE-NE	Department of Energy Nuclear Energy
DWPF	Defense Waste Processing Facility
EDS	energy dispersive spectrometry
EPA	Environmental Protection Act
FY	Fiscal Year
HIP	hot isostatic pressing
HLW	high level waste
HUP	hot uniaxial pressing
LLNL	Lawrence Livermore National Laboratory
MC&A	material control and accountability
MOX	mixed oxide (fuel)
NDE	nondestructive evaluation
NRC	Nuclear Regulatory Commission
OCRWM	Office of Civilian Radioactive Waste Management
PIP	Plutonium Immobilization Plant
PNNL	Pacific Northwest National Laboratory
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RD&T	research, development, and testing
REE	rare earth element
SEI	secondary electron image
SEM	scanning electron microscopy
SPFT	single-pass flow-through
SRS	Savannah River Site
SYNROC	synthetic rock
TEM	transmission electron microscopy